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Item 6 (j) of the provisional agenda*

Matters for consideration or action by the Conference of the Parties: effectiveness evaluation

Guidance for a global monitoring programme for persistent organic pollutants

Note by the Secretariat

The annex to the present note contains information provided by the United Nations Environment Programme. The annex has not been formally edited.

* UNEP/POPS/COP.1/1.

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Annex

UNITED NATIONS ENVIRONMENT PROGRAMME

CHEMICALS

UNEP

Guidance for a Global Monitoring Programme for Persistent Organic Pollutants

1st edition
June 2004

Prepared by UNEP Chemicals
Geneva, Switzerland

IOMC INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS
A cooperative agreement among UNEP, ILO, FAO, WHO, UNIDO, UNITAR and OECD

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This publication was financed by Canada through the Canadian POPs Trust Fund and is produced within the framework of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC).

The Inter-Organization Programme for the Sound Management of Chemicals (IOMC), was established in 1995 by UNEP, ILO, FAO, WHO, UNIDO and OECD (Participating Organizations), following recommendations made by the 1992 UN Conference on Environment and Development to strengthen cooperation and increase coordination in the field of chemical safety. In January 1998, UNITAR formally joined the IOMC as a Participating Organization. The purpose of the IOMC is to promote coordination of the policies and activities pursued by the Participating Organizations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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Foreword

The effectiveness of the Stockholm Convention on Persistent Organic Pollutants (POPs) shall be evaluated within four years of entry into force of the Convention, i.e. before 17 May 2008. In order to perform a scientifically sound and meaningful evaluation based on comparable monitoring data of the twelve POPs under the Convention all available data from existing national, regional and global monitoring programmes should be considered.

Most present programmes focus on a restricted part of the globe e.g. the Great Lakes, the Baltic, the North Sea or the Arctic. For large areas, even whole continents, particularly those with a large proportion of developing countries, data on levels of POPs in relevant media are few or non-existent.

To support the effectiveness evaluation of the Convention UNEP Chemicals has initiated an activity that aims at providing the tools for countries and regions where POPs monitoring programmes are poorly developed or non-existing to develop such programmes in a consistent and cost-effective way. This would promote comparability and contribute substantially to the development of a global picture of POPs. In the longer term it is hoped that new and existing programmes may evolve towards increased similarity.

Our aim is that this guidance document would become an important tool to assist countries and regions in setting up regional structures to monitor POPs as well as in modifying existing programmes. In developing new programmes or strengthening existing ones all available data should be used to the greatest extent possible. Programmes should also be set up in the most cost-effective way possible, taking into account socio-economic and policy considerations. In view of the rapid evolvement of science and technology in this and related areas the guidance should be regarded as a working document to be tested and revised based on experience.

UNEP Chemicals wishes to thank all the experts that have contributed to this effort and looks forward to feed back from users and others who are interested in the development of POPs environmental monitoring.

ABBREVIATIONS AND ACRONYMS

AMAP	Arctic Monitoring and Assessment Programme
ANCOVA	Analysis of Covariance
ANOVA	Analysis of Variance
BCF	Bioconcentration Factor
CITES	Conference on International Trade in Endangered Species
COP	Conference of the Parties (to a Convention)
CRM	Certified Reference Material
DDD	Metabolite of DDT
DDE	Metabolite of DDT
dw	Dry weight
ECEH	European Centre for Environment and Health
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe
EPA	Environmental Protection Agency
FAO	Food and Agriculture Organisation of the United Nations
GAW	Global Atmosphere Watch
GCG	Global Co-ordinating Group
GEF	Global Environment Facility
GEMS	Global Environment Monitoring System
GMP	Global Monitoring Programme
HELCOM	Helsinki Commission/The Baltic Marine Environment Protection Commission
ICES	International Council for the Exploration of the Sea
IMO	International Maritime Organisation
INC	Intergovernmental Negotiating Committee
IPCS	International Programme on Chemical Safety
LOD	Limit of Detection
LOQ	Limit of Quantitation
LRM	Laboratory Reference Material
LRTAP	Long Range Transboundary Air Pollution Convention (under the auspices of UNECE)
LTER	Long Term Ecological Research
MDL	Method Detection Limit
NGOs	Non-Governmental Organisations
OC	Organochlorine
OCP	Organochlorine Pesticide
OECD	Organisation for Economic Co-operation and Development

OSPAR	Oslo Paris Commissions, Convention for the Protection of the Marine Environment of the North East Atlantic
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo-*para*-dioxins
PCDF	Polychlorinated dibenzofurans
POPs	Persistent Organic Pollutants
PTS	Persistent Toxic Substances
PUF	Polyurethane Foam
RIG	Regional Implementation Group
SOP	Standard Operating Procedure
SPMD	Semi-permeable Membrane Device
STAP	Scientific and Technical Advisory Panel
TCDD	Tetrachlorodibenzo-*para*-dioxin
TEF	Toxic Equivalency Factor
TEQ	Toxicity Equivalents
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
WHO	World Heath Organisation
WMO	World Meteorological Organization

CONTENTS

1 BACKGROUND AND OBJECTIVES

The Stockholm Convention on POPs (UNEP, 2001) (Persistent Organic Pollutants) entered into force 17 May 2004. As of 14 June 2004 the convention has 66 Parties. The first session of the Conference of the Parties (COP) is scheduled to take place 2-6 May 2005 in Punta del Este, Uruguay. The major features of the Convention are summarised in "Ridding the world from POPs" (UNEP, 2002), a layman's guide to the Stockholm Convention available in the six UN official languages.

The objective of the Stockholm Convention on POPs is to protect human health and the environment from the persistent organic pollutants, taking into account the precautionary approach as stated in the Rio Declaration. Parties have agreed that they need a mechanism to measure whether this objective is reached. According to Article 16 of the Convention its effectiveness shall be evaluated starting four years after the date of entry into force of the Convention and periodically thereafter at intervals to be decided by the COP.

In order to facilitate such an evaluation, the COP shall, at its first meeting, initiate the establishment of arrangements to provide itself with comparable monitoring data on the presence of the chemicals listed in Annexes A, B and C of the Convention as well as their regional and global environmental transport. The evaluation shall be conducted on the basis of available scientific, technical and economic information, including e.g. reports and other monitoring information.

To facilitate the effectiveness evaluation under the Stockholm Convention UNEP Chemicals has initiated an activity that aims at linking together existing national, regional and global activities on POPs monitoring. In many countries and regions the capacity and capability to participate fully in such a programme is lacking. Capacity building and transfer of technology and know how is needed to improve the situation.

The primary focus of the effectiveness evaluation will be on comparable monitoring data on the presence of the POPs listed in Annexes A, B and C of the Convention as well as their regional and global environmental transport. To develop recommendations in this field UNEP Chemicals hosted a Workshop to Develop a POPs Global Monitoring Programme (GMP) to Support the Effectiveness Evaluation of the Stockholm Convention on POPs, held in Geneva from 24 to 27 March 2003 (UNEP, 2003). The outcome of the workshop was a set of conclusions and recommendations for the elements to be contained within a global programme. The present Guidance Document is based on the recommendations of that workshop.

There is a need to get an overview of laboratory capacity for POPs analysis worldwide. Work is ongoing by UNEP Chemicals to create an inventory of POPs laboratories, which will also provide information on the technical and analytical capabilities of each laboratory so that potential partners for a POPs GMP may be identified. The inventory is available on the POPs GMP website.

Similarly, there is a need to assess the feasibility of setting up a regional structure for measuring POPs in developing country regions. The Global Environmental Facility (GEF) has recently approved a Medium Size Project on Assessment of Existing Capacity and Capacity Building Needs to Analyse POPs in Developing Countries. In addition to assessing

the feasibility of a regional structure for POPs analysis the project will include testing of the guidance document and its applicability in one or several regions. The Government of Canada has generously provided funding of $250,000 for a pilot study in one region and the Government of Germany has committed €150,000 for a pilot study in another region.
The present Guidance Document should be seen in this broader context. It is the intention of UNEP Chemicals to test the document in its final draft format in the second phase of the GEF project mentioned above. The Guidance Document would hopefully also be of value for the laboratories identified through the inventory building process and would assist them in developing their capacity as well in preparing targeted proposals for support from their government or from other donors.

It is hoped that in providing a consistent and comprehensive framework for global POPs monitoring the guidance document would guide existing monitoring programmes in their planning of future activities.

This document should be regarded as work in progress. Based on the experiences from the testing of the document in developing country regions it would be revised and updated before being published in its final format.

The guidance document has been prepared by a group of experts with the following composition:
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The expert group has met twice during the development of the document under the chairmanship of Dr. Bo Wahlström, Senior Scientific Advisor, UNEP Chemicals. Comments have been received throughout the process from the POPs Advisory Group (see appendix). The input from Dr. Frank Wania, Dr. Pierrette Blanchard and Dr. Tom Harner to chapter 4.1 on Air is gratefully acknowledged. The experts also wish to acknowledge the strong scientific foundation laid by the participants to the March 2003 POPs Global Monitoring Workshop. Finally thanks go to Dr. Linn Persson, UNEP Chemicals, for editing and formatting the report for final publication.

1.1 The objectives of a POPs global monitoring programme

The objective of the POPs global monitoring programme (GMP) is to:

> Provide a harmonized organisational framework for the collection and assessment of comparable monitoring data on the presence of the POPs listed in Annexes A, B and C of the Convention in order to identify temporal and, as appropriate, spatial trends as well as to provide information on their regional and global environmental transport.

The COP has the responsibility for establishing the arrangements to obtain necessary information on environmental levels, but it is the Parties who bear responsibility for implementation. Article 16 points towards regional implementation and to the use of existing programmes to the extent possible. This Guidance Document has been prepared as the initial step to ensure the required level of harmonization.

1.2 The objectives of the Guidance Document

To complete an assessment based upon comparable information on environmental background levels, the monitoring programme must provide guidance on (for example) how information is to be collected, analyzed, statistically treated and assessed. This guidance must also accommodate in some cases using existing programmes and in other cases the setting up of new activities. It must also describe a harmonized regime for the assessment. The objective of this Guidance Document is therefore to:

> Provide a uniform framework for all activities associated with collection, assessment and reporting of environmental background levels of POPs in order to provide comparable information for the COP as required in Article 16 of the Convention.

It is expected that the Guidance Document will provide a living framework, that is, one that may evolve and be elaborated over time to reflect experience and emerging specific needs. The present Guidance Document is based upon recommendations provided by a Workshop held in Geneva from 24 to 27 March 2003, and further developed through expert consultation. The full workshop report is available (UNEP 2003). A summary was presented at the sixth session of the Intergovernmental Negotiating Committee (UNEP/POPs/INC.7/20), at which time the Secretariat was requested to prepare the Guidance Document for consideration at the first meeting of the COP.

1.3 General principles

In developing the global POPs monitoring, a number of general principles have been applied. They are presented here because of their potential to assist in decision making in the regional and global context as the programme becomes operational.

- The programme strives for simplicity and, to the extent possible, builds on existing programmes to meet present and future needs. It encourages plasticity, which is the ability to evolve over time in order to respond to the needs of the Convention while maintaining comparability. Plasticity is enhanced by simplicity of the original design.

- Clarity of design should be promoted for the sampling activities; of expectations for standards of analytical performance; and of arrangements for QA/QC.

- Differences in capacity within and between regions provide opportunities for regional capacity building focused to ensure a capability to detect regional trends. In order to put the GMP into regional reality, capacity building will be a crucial aspect for implementation. In keeping with the regional approach proposed for the GMP, capacity building under this programme should be include the following elements: a)

institutional capacity, ensuring long-term sustainability of monitoring efforts; b) laboratory and technological capacity; and c) human capacity comprising professional and technical expertise. Sustainability is strongly linked to both simplicity and effectiveness.

- Only the substances contained in Annexes A, B and C of the Convention are considered in the context of Article 16. The environmental levels of the annex substances are measured primarily in order to detect changes over time, which is essential for effectiveness evaluation. The focus is therefore upon background levels of POPs at locations not influenced by local sources.

- It is essential to cherish inclusiveness and transparency in all aspects of the programme design, conduct and in the assessment process. Failure risks a lack of confidence and interest in the final reports.

- Monitoring for effectiveness evaluation (Article 16, paragraph 2) will not address: issues of compliance; preparation of dossiers for substances that may be proposed for addition to the Annexes; hot spot detection and evaluation; or, specific issues of scientific understanding.

1.4 Outline of the strategy for the assessment

It is proposed that the GMP for POPs be comprised of "Regional" and "Global" organisational elements. Regional information gathering and assessments would be planned, organised, and implemented on a regional basis following an agreed global framework. Regional assessments, again following an agreed global format, would provide the basis for a global assessment report. A diagrammatic representation of the organisational structures and arrangements suggested in this section is presented in Figure 1.1 in a chronological order to illustrate the roles to be performed over time.

The recently completed Regionally Based Assessment of Persistent Toxic Substances (GEF/UNEP 2000/3) is particularly instructive on the organisational matters. This project was not concerned with monitoring but aimed (*inter alia*) to provide a regionally based global assessment of persistent toxic substances in the environment, their concentrations and impact on biota, and their transboundary transport. A series of regional assessments were produced within the regions by teams of regional experts, each following an over-all global strategic framework of procedure. The regional assessments were accompanied by a single global overview document (GEF/UNEP 2000/3). It therefore faced many of the challenges that lie ahead for the global monitoring of POPs.

1.4.1 The regions

A number of options have been considered to provide the basic regional structure for the programme. The option proposed is for the adoption of a structure based upon that of UNEP and of the five regional commissions of the United Nations. These are: Africa; Asia and the Pacific; Central and Eastern Europe; Latin America and the Caribbean; and Western Europe and North America.

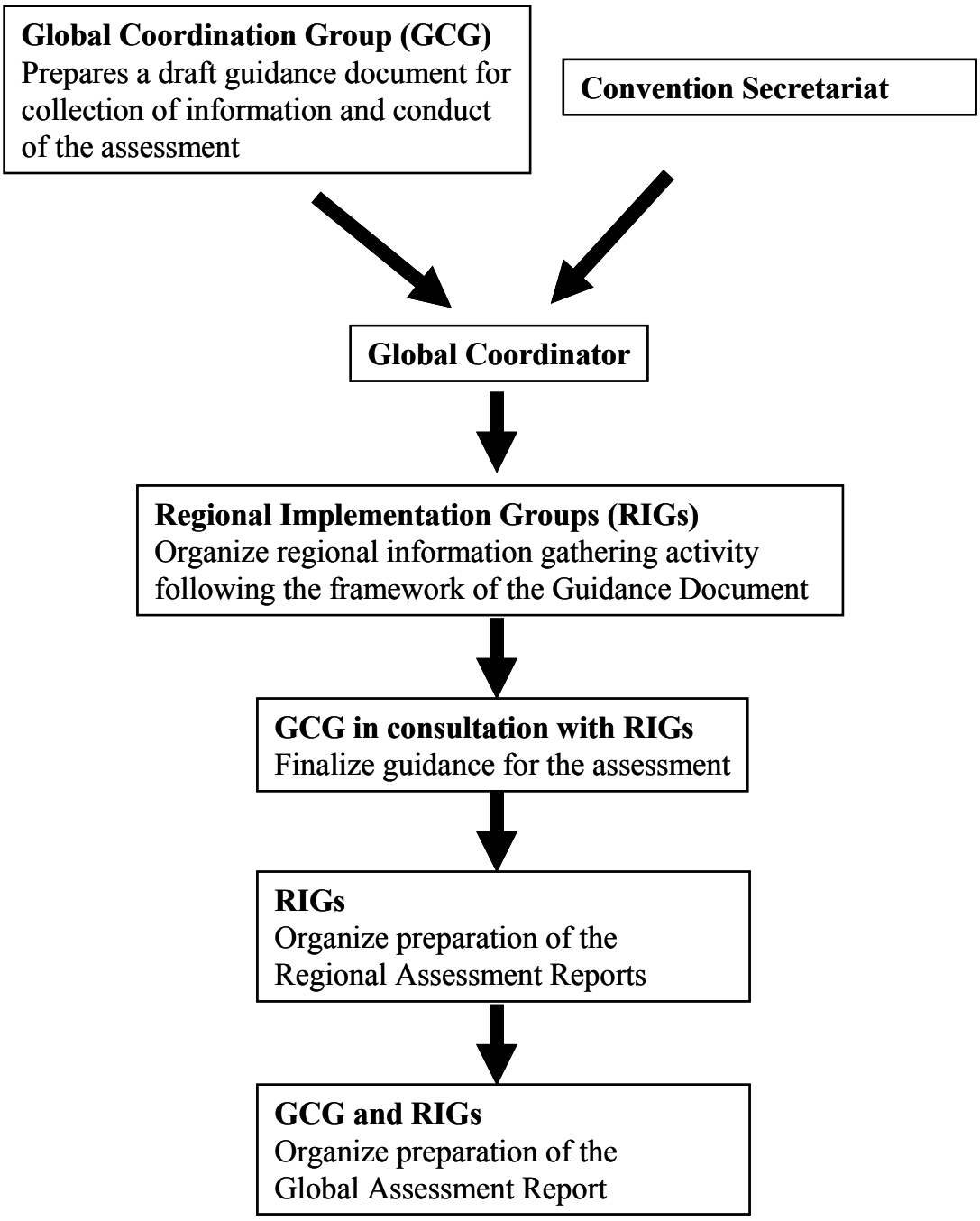

Figure 1.1 Proposed organisation structure and activity flow leading to completion of the assessment reports.

This scheme has been supported because it: offers an optimal combination of using existing regional structures which already possess organisational support; affords good opportunities for capacity building and technology transfer within and between regions; and, would be parallel to the organisation of UNEP Chemicals, thus facilitating assistance from that organisation.

Within each region, all activities would be under the direction of a "Regional Implementation Group" (RIG). Sub regional arrangements that take into account linguistic, political and geo-physical considerations could be introduced to further support the organisation of the work. Twinning and partnerships between regions would be encouraged.

Special arrangements can be undertaken on a case by case basis when pre-existing programmes have a different regional system from that described above.

1.4.2 Global strategy for information gathering

Under the proposed scheme, a team of managers/experts here called the Global Co-ordinating Group (GCG), would provide oversight for the gathering and assessing of information on the environmental levels of POPs to be used for the effectiveness evaluation. Their duties would include *inter alia*:

- Structuring of the monitoring network;
- Protocols for QA/QC, sample collection, and analytical methodologies;
- Protocols for data archiving and accessibility;
- Protocols for trend analysis methodologies;
- Establishing the information needs and methodology of the regional and global environmental transport assessment;
- Establishing the criteria for composition of the RIGs, see below;
- Maintenance of interaction with all the RIGs; and,
- Developing elements to encourage capacity building;

1.4.3 Regional strategy for information gathering

A RIG would be established in each region to be responsible for implementing the global guidance document within that region, taking into account regional realities. The regions would be the operational units for data and information gathering, analysis, and assessment. Their duties would include *inter alia*:

- Establishing their membership;
- Structuring of the regional monitoring network;

- Organizing sampling and analytical arrangements;
- Ensuring compliance with protocols for QA/QC, sample collection, analytical methodologies; data archiving and accessibility; and for trend analysis methodologies;
- Maintenance of interaction with the GCG and with other RIGs as appropriate;
- Developing elements to encourage capacity building; and,
- Identifying where existing suitable monitoring data are and are not available. Two important tools are the Regionally Based Assessment of Persistent Toxic Substances, and the fifth edition of the Master List of Actions on the Reduction and/or Elimination of releases of POPs (UNEP/POPS/INC.7/INF/15).

The final product of the RIG under this element would be an operational regional monitoring programme and a regional assessment report. The regional reports would serve two purposes. Individually they would inform the COP on regional levels of POPs and collectively, they would provide the technical basis for completion of the global assessment (to be organised by the GCG).

1.4.4 Global strategy for regional and global assessment activities

It is anticipated that the final product of the GMP would be a compendium of regional assessment reports, one for each region, together with a global overview report. Under the proposed scheme, they would be produced as follows:

Regional assessments: Each RIG would oversee the production of a substantive regional assessment prepared by a drafting team of experts selected by the RIG for that particular region. These assessments would be the main means by which the COP would be informed of the regional trends and transport of POPs in the environment.

Global assessments: The global report would be produced by a drafting team of experts under the purview of the GCG. The team should also contain individual experts drawn from the writing teams of the regional assessments.

Global and regional guidance for the assessment reports: It is envisaged that when the COP has approved the arrangements for the GMP, the GCG in consultation with the RIGs would produce a supplement to the Guidance Document which would elaborate detailed guidance for the preparation of the regional and global assessment reports. It would include *inter alia*:

- A common strategy for the completion of the regional, and global assessments;
- An annotated structure for each type of report (Regional, Global, and Environmental transport). An indicative first draft outline structure for the reports is included in the Annex A;

- An outline of the accountabilities and responsibilities for those involved in the assessment; and,

- The information needs, proposed methodology, and expected deliverables of the regional and global environmental transport assessment;

It is suggested that when organizing and conducting the assessment process, the RIGs and the GCG would undertake arrangements to promote the following:

- A clear understanding of data ownership. Intellectual property difficulties have arisen in other comparable programmes;

- The importance of assurance of unencumbered access to data and to supportive information (e.g. age or sex of species from which samples may have been taken) required for the assessment;

- A uniform understanding by all members of the assessment teams on the objectives of the task; and,

- The necessity for clear accountabilities for those involved in the assessment. This is particularly important given the regionalization of the assessment process.

1.5 Other information sources

During the assessment process, the assessment teams should be able to use information derived from sources external to the GMP, providing that quality standards are not compromised. To assess the capacity of existing monitoring programmes, the interim Secretariat has opened discussions with organisations such as the World Health Organization, and other data producers and providers regarding access to information. When appropriate, memoranda of agreement with such organisations have or can be developed.

Article 11 of the Convention is concerned with the conduct of research and monitoring aimed to improve the basic understanding of such characteristics as the sources, movement, fate, behaviour and toxicity of POPs in the environment. These activities which can be conducted at any level of organisation (e.g. national, regional or global) and are not restricted to the substances listed in the Convention are not formally linked to effectiveness evaluation. However it is possible that information resulting from such activity could be of assistance in the preparation of the Article 16 assessments.

Article 16 does not specifically exclude non-parties from contributing information. Countries that have signed the Convention, but are not yet Parties, would be encouraged to provide information, which conforms to the framework described in this document. However, countries participating in this way would be “passive” contributors and would not be able to take part in decision making, or be members of the writing team for the periodic assessments.

1.6 Arrangements to address global and regional environmental transport

Paragraph 2 of Article 16 states that the arrangements to be established to provide the COP with comparable monitoring data on the presence of the chemicals listed in the annexes, should also inform the COP on their regional and global environmental transport. Therefore this need should also be provided for by the GMP. It is proposed that as soon as the COP has adopted the GMP, the GCG and the RIGs would develop a supplement to the Guidance Document which would describe a guidance framework for the transport elements of the assessment. This guidance would include a description of:

- The discrete objectives of Article 16. The GMP is not being established to provide a comprehensive understanding of the environmental behaviour of the POPs listed in the Annexes of the Convention.

- What it is envisaged would be the optimal deliverables for the COP concerning the global and regional transport elements, bearing in mind also the budgetary concerns expressed at several sessions of the Intergovernmental Negotiating Committee (INC).

- What are the data, and the analytical and assessment tools required to support the optimal deliverables.

- The present capabilities of a variety of tools developed by the scientific community that can assist in demonstrating the long-range transport of POPs. Many involve models (e.g. Shatalov, 2001; and as summarized for example in Scheringer and Wania, 2003; OECD, 2002; and AMAP, 1999). Regional fate and transport models can aid in the analysis of the observational data generated by the GMP, in particular with respect to the quantification of regional and global transport. Other less demanding methods employ back trajectory analysis (e.g. Bailey *et al*., 2000).

- Assessment of the existing extensive scientific research effort on the regional and global transport of POPs may be utilized.

- The concerns expressed by the INC with respect to costs. Therefore it is important that in developing arrangements, new activities to service the assessment should only be undertaken if such tools can be shown to be essential for effectiveness evaluation.

Some recommendations derived from the global consultations have already been elaborated in this document. For example, the global distribution of POPs in all environmental media primarily stems from their ability to move quickly in the atmosphere with cycles of successive partitioning between air and other media. Therefore whatever may be decided upon regarding deliverables, the collection of air samples from sites not impacted by local sources and from which good meteorological information is available would be a necessity. This was one of the primary considerations in the consultation process recommending that air should be one of the key media monitored in the POPs GMP and these needs are anticipated in those sections relating to air in the present Guidance Document.

A conceptual approach that may be taken by the GCG and the RIGs when developing their guidance is to consider the issue from the viewpoint of a “mock transport assessment team”.

This will help to identify the range of practical products for this component of the assessment before moving to identify the data, tools and methods required to complete the task.

It has been noted that the Global Report of the Regionally Based Assessment of Persistent Toxic Substances (GEF/UNEP 2000/3) included an assessment of knowledge on the long-range transport of these substances. The structure used in that study is considered to have functioned well and it is suggested that it could provide a first draft structure for a single transport report to serve both regional and global transportation elements required under Article 16. This structure is provided in the Annex A without modification.

Work is ongoing by UNEP Chemicals to create an inventory of POPs laboratories, which will also provide information on the technical and analytical capabilities of each laboratory so that potential partners for a POPs GMP may be identified. The inventory is available on the POPs GMP website.

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2 SUBSTANCES TO BE MONITORED

2.1 Background

The ultimate goal of the Stockholm Convention is to decrease the concentration of POPs in the environment and man. An obvious way to evaluate the effectiveness of the Convention is thus to measure the concentration of the listed chemicals in these matrices. The substances or groups of substances listed in the Convention are:

- Aldrin
- Chlordane*
- Dieldrin
- Endrin
- Heptachlor
- Hexachlorobenzene (HCB)
- Mirex
- Toxaphene*
- Polychlorinated biphenyls (PCB)*
- Dichlorodiphenyltrichloroethane (DDT)*
- Polychlorinated dibenzo-*para*-dioxins (PCDD)*
- Polychlorinated dibenzofurans (PCDF)*

Substances marked with an asterix are mixtures of several congeners, for some of them several hundreds. It is not necessary, or even possible, to analyse all these congeners and this chapter will try to give guidance on useful strategies, section 2.3 suggests possible cost-effective alternatives.

2.2 Recommendations from the GMP workshop in May 2003

The experts attending the GMP workshop in May 2003 recommended that prevailing levels for all twelve POPs should be determined initially at background sites in all regions and then individual regions may establish priorities for further analysis. The group also recommended the compounds to be analyzed, including several congeners for the mixtures and also some degradation products. They identified two ambition monitoring levels, essential and recommended. The result is given in a table in the proceedings from the workshop, and compounds regarded as essential to monitor can be seen in Table 2.1.

Table 2.1. Essential analytes for the determination of POPs recommended by the GMP workshop in May 2003.

Chemical	Analytes
HCB	HCB
Chlordane	*cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor, oxychlordane
Heptachlor	Heptachlor, heptachlorepoxide
DDT	4,4'-DDE, 4,4'-DDD, 4,4'-DDT
Mirex	Mirex
Toxaphene	Congeners P26, P50, P62
Dieldrin	Dieldrin
Endrin	Endrin
Aldrin	Aldrin
PCB	ΣPCB_7 (congeners 28, 52, 101, 118, 138, 153, and 180)
	PCB with TEFs*: (12 congeners: 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189)
PCDD/PCDF	2,3,7,8-substituted tetra- to octachlorodibenzo-*p*-dioxins and dibenzofurans (17 congeners)

* PCB with TEFs (Toxic Equivalency Factors) are those congeners that have been found to have dioxin-like effects.

As many of these compounds have similar properties they can be determined in the same analytical procedure (see also Chapter 5).

2.3 Further prioritisation

Temporal trends have to be determined for the evaluation of the Convention. In most cases this means that small differences between samples from different years have to be found, and thus the highest analytical accuracy (or at least reproducibility) is needed. Looking at the list of analytes recommended in Table 2.1 there are many different substances to be determined. Ideally, all should be determined in all samples, but the high costs of analyses of PCDD/PCDF and PCB with TEFs will probably make it necessary to apply these to a limited number of samples. Several biochemical methods are available to screen samples for dioxin-like effects, and those can be used to select the samples for analyses.

A further prioritisation may be necessary in some regions, and this may be based on the levels of the different POPs in the region. Any existing data can be used for this priority

setting, and a recent compilation was done in the project "Regionally based assessment of persistent toxic substances" (PTS). For example, mirex may not be present at detectable concentrations, and may thus be excluded from the list of monitored substances, and according to Annex A of the Stockholm Convention endrin is neither produced nor used in any region today. The possibilities, and economic advantages, of using indicator substances for a group (e.g. PCB 153 for PCB) in some matrices could also be regionally investigated.

2.4 References

Web references:

GMP workshop, 2003 http://www.chem.unep.ch/gmn/Files/popsmonprg_proc.pdf

PTS http://www.chem.unep.ch/pts/default.htm

3 STATISTICAL CONSIDERATIONS

The aim of this chapter is to review the statistical requisites that must be satisfied if a monitoring program is to meet the objectives set out in Chapter 1.

3.1 Quantitative objectives

Describing and carefully defining the objectives are the most crucial step in planning and organizing monitoring activities. It includes the choice of sampling matrices and strict definitions of sampling units and a description of what they represent in time and space. This description is a prerequisite for an appropriate interpretation of the results.

However, in order to properly estimate e.g. number of samples per sampling occasion, length of the time-series, sampling frequency etc, required for the investigation, quantitative objectives have to be defined. Quantitative objectives imply that the required sensitivity of the program is stated, i.e. that the smallest change for temporal studies or smallest difference between areas for geographical studies is specified together with the required statistical power to detect such a difference.

A quantified objective for temporal studies could thus be stated for example like this:
To detect a 50 % decrease within a time period of 10 years with a power of 80 % at a significance level of 5 %. (A 50 % decrease within a time period of 10 years corresponds to an annual decrease of about 7 %).

And for spatial studies e.g. like this:
To detect differences of a factor 2 between sites with a power of 80 % at a significance level of 5 %.

Furthermore, in order to calculate e.g. the number of samples and the sampling frequency required to fulfil these objectives, an estimate of the sample variance is needed. Expected variance estimates could maybe be extracted from similar ongoing monitoring programmes or, more reliable, be assessed from a pilot project using the same sampling strategy, sampling matrices etc as the currently planned monitoring programme. In order to optimise the programme from a cost-benefit point of view, all costs for e.g. sampling, sample preparation and chemical analysis must be specified.

3.2 Representativity

It is essential that the suggested matrices are thoroughly described concerning what they represent in relation to pollution load or exposure. Apart from factors like availability, sampling costs etc information on e.g. concentration factors, bioaccumulation rates, metabolic capacity, and excretion rates. Various tissues within the same species varies considerable in respects of the above-mentioned factors i.e. they may represent totally different ranges of time and they may react to changes in the environment very differently.

Even though these questions are not purely interesting from a statistical point of view they will constitute invaluable pieces in the building of a modelling framework to enable an integrated assessment of contaminant load and exposure from various matrices.

Using mammals or species with a more or less developed capacity to degrade POPs may lead to spurious results. Elevated levels of one POP may trigger and enhance the metabolic capacity to degrade other POPs. This may cause a problem e.g. to evaluate spatial differences in POP exposure from human milk (Weiss *et al*., 2003).

3.3 Sources of variation

There are numerous factors that affect measured concentration in environmental samples other than those of anthropogenic origin. For monitoring programmes that are designed to assess the effects of measures taken to reduce discharges of contaminants from industrial activities or control by means of pesticides, these factors can be considered as confounding factors. Avoiding or adjusting for confounders can improve statistical power in monitoring programmes considerably (e.g. Grimås *et al*., 1985; Nicholson *et al*., 1991b; Bignert, 2002).

Seasonal variation for several POPs (e.g. PCB, PCDD/PCDF, DDTs and HCB) has been demonstrated. The reasons could be both a seasonal variation in the discharge pattern from the sources and be due to e.g. physiological factors like spawning etc. If the main objective is to monitor the mean change in pollution load rather than to investigate the seasonal pattern in the discharges, sampling should be restricted to one season (the most favourable season from a minimum random variation point of view) in order to gain statistical power. The same arguments could be addressed if a diurnal pattern is discernible for fast changing matrices like air.

Fat content and composition in human milk changes dramatically during the first weeks after birth, which leads to variation also in analysed POPs (e.g. Weiss *et al*., 2003). In order to reduce random variation, sampling should preferably be carried out during a well defined period three weeks after birth (Also the fat content varies considerably depending on if sampling is carried out in the beginning or at the end of the feeding session).

Other known or suspected confounding factors possible to control for at sampling (e.g. age and sex) should be specified in the monitoring guidelines. In order to decrease sample variation younger specimen most often show a smaller between specimen variance compared to older specimens of the same species. This may generally be explained by the fact that younger individuals are more stationary and that the metabolic capacity is less variable in younger specimens. Thus, the permitted range in age should be kept as narrow and as low as possible, but still of course, allowing for homogenous samples with a sufficient number of individuals within the same age class from year to year and also secure that a sufficient amount of sample tissue can be extracted for chemical analyses. Biota samples should preferably be restricted to one sex.

The use of narrow sampling unit definition implies that a smaller part of the studied population is represented. Often, this leads to unfounded assumptions of similar trends e.g. for both sexes or for various age classes. To improve representativity, if economy permits, stratified sampling should be applied rather than allowing for a wider definition of the

sampling unit. General aspects of sampling design, applicable also for monitoring, are discussed e.g. by Underwood (1993, 1994, 1996).

The precision of chemical analysis is generally believed to constitute only a minor part of the total variance in monitoring time-series of environmental data where sample variation is expected to be large, much larger compared to laboratory conditions. This is true if the same accredited laboratory is used through the whole series. However, if different laboratories from year to year carry out the analysis, this could seriously decrease or disable the possibility to evaluate time-series of e.g. POPs. The same is true if the same laboratory changes its methodology and, for example, co-elutions are resolved leading to a decrease in estimated concentrations unless measures are taken to compensate for this. If detection limits are improved, i.e. analytes are now found where they were not detected before, this may lead to similar problems depending on how 'less-than-concentrations' are treated.

Provided that individual samples are taken and that appropriate confounding variables are registered or measured at the chemical analysis, the concentrations may be adjusted for varying covariates by means of e.g. ANCOVA (Analysis of Covariance). This may improve the power to detect changes over time or differences among sites considerably (Bignert, 2002). Furthermore, the detection and possible elimination of erroneous extreme values would also noticeable improve the power (Barnett and Lewis, 1994; Nicholson *et al*., 1998; Bignert, 2002).

3.4 Length of time-series

It can be shown that several well-established monitoring programmes have surprisingly low power to detect temporal changes of significant importance (Nicholson and Fryer, 1991; Bignert *et al*., 2004). It is naïve to expect monitoring time-series of POPs to reveal changes with any confidence within a sampling period of five years unless the changes are very large. More likely, we would expect at least 10-15 years to detect changes of moderate size (5 % / year).

A study would need at least 4-5 years of monitoring to give reliable estimates of random within- and between-years variation and other components of variance. This information would be invaluable for the improvement and tuning of the on-going monitoring activity.

It should be stressed that even for spatial studies a few years of sampling is not enough but can lead to spurious results (Bignert *et al*., 1994).

3.5 Number of samples needed

Larger samples provide more precise and reliable estimates of mean concentrations and variance. However, the contributions from additional samples depend to a very high degree on the sampling strategy.

To estimate the number of samples needed in an appropriate way for a certain situation, quantitative objectives must be defined and information on expected variance must be available (see above). The standard formulas for calculating the number of samples needed assume independent observations. In many typical monitoring situations this assumption is

not altogether true. Small-scale variation in time and space may not be covered by the sampling scheme which leads to an underestimated variance and increased between-year variation e.g. Bjerkeng (2000) showed that by sampling at three occasions during the sampling period instead of one and using the same number of samples or less, the yearly mean variance estimate could be reduced by up to 65%. Furthermore, stratified sampling and the choice between individual and pooled samples will affect the estimates of the required number of samples. Without the information mentioned above, no optimal figures on the required number of samples can be calculated.

Using pooled samples of several specimens will decrease the number of chemical analyses required to estimate a reliable mean concentrations compared to individual samples since a larger proportion of the total population is represented. Disadvantages with pooled samples are that extreme values from single specimens may influence the concentration of the pool without being revealed, and that the possibility to adjust for confounding variables or correlate with biological effects disappears. Information on individual variance within a year has also a value in itself. An increased variance is often the first sign of elevated concentrations. Especially in the first stage of establishing a new sampling site, individual samples could help to reveal possible sources of variation. A more detailed discussion of advantages and disadvantages with individual versus pooled samples is given by Bignert *et al.* (1993).

For temporal trend studies of contaminants in fish, the guidelines for both OSPAR and HELCOM recommends 12 individual samples per year unless stratified sampling is used (HELCOM, 1998). Simulation studies show that decreasing the annual number of samples, in time-series of POPs measured in fish, from 25 to 12 individual samples per year will cause only a minor decrease in statistical power whereas a number less than 10 will imply considerably reduced power to detect changes of reasonable magnitude.

3.6 Sampling frequency for temporal trend studies

To determine an appropriate sampling frequency, the required temporal resolution has to be specified. To monitor certain events or incidents with a short time lapse, sampling may have to be carried out very often during certain periods. Considering e.g. the half time for POPs in biological tissues, analytical cost etc, sampling once or, at most, twice per year is generally appropriate for monitoring of contaminants in biota. (However, sampling at several occasions during the sampling period to cover small scale temporal variation will improve the mean estimate, as has been pointed out above). The examples above refer to sampling once a year.

Obviously the statistical power of a trend-test is seriously reduced when sampling with a lower frequency. An illustrative example is given in Figure 3.1a showing development over time for total PCB in herring in the southern Baltic Proper based on annual collected data. In Figure 3.1b, sampling each third year, starting in 1972, 1973 or 1974, respectively, is simulated resulting in three completely different trends.

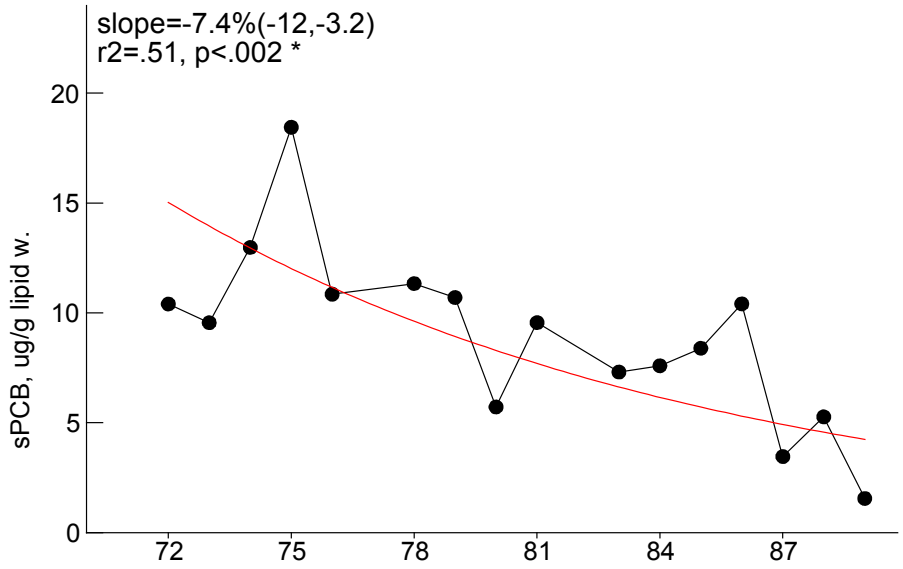

Figure 3.1a Annual mean concentration of total PCB (µg/g lipid weight) in young herring collected during the breeding season 1972-1989 in the Karlskrona archipelago and a log-linear regression line (redrawn from Bignert *et al.,* 1993).

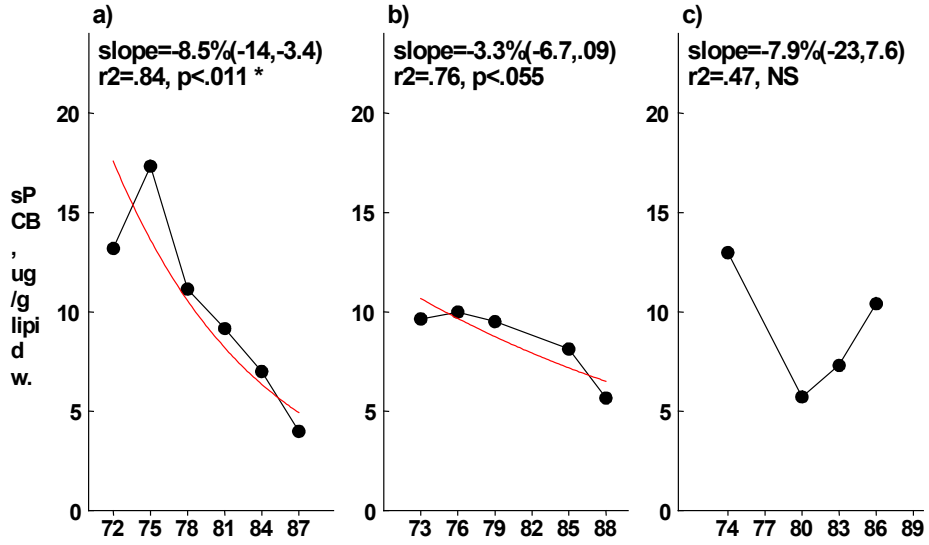

Figure 3.1b Annual mean concentration of total PCB (µg/g lipid weight) in young herring collected during breeding season in the archipelago of Karlskrona and log-linear regression lines where $p < 0.1$. The three examples demonstrate the time-series that would be obtained if sampling were performed every three years starting in 1972, 1973 and 1974, respectively (redrawn from Bignert *et al.* 1993).

If the length of a time-series is fixed, the power for various slopes at a certain between-year variation can be estimated. Figure 3.2 shows the relation between power and slope (e.g. the change in time-series of POPs measured in biota samples), estimated at sampling every, every-second, third and fourth year, respectively, at a standard deviation (between-year

variation) along a regression line of 0.20 on a log-scale (a relatively low standard deviation among the time-series of the Swedish monitoring programmes of contaminants in biota). If the desired sensitivity of the monitoring programme is to be able to detect an annual change of, at least 5% per year within a time period of 12 years, the power is almost 80% for sampling each year at this standard deviation (Figure 3.2). For sampling every second, third or fourth year the corresponding power is only approximately 35, 17 and 10%, respectively.

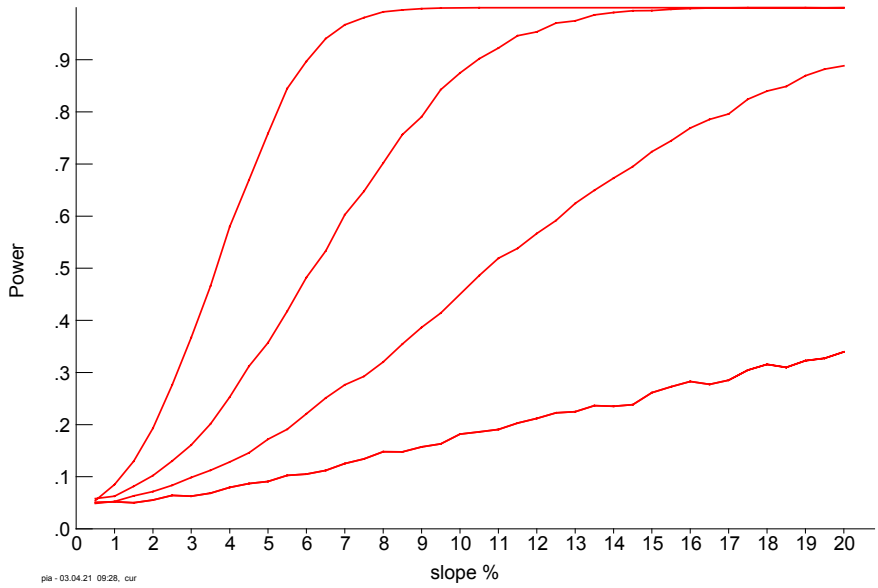

Figure 3.2 Power as a function of slope (annual change in %) at log-linear regression analysis (two-sided, α=0.05) for a sampling period of 12 years at a residual standard deviation on a log-scale of 0.20, assuming normally distributed residuals. The graphs, from left to right, represent sampling every, every-second, third and fourth year, respectively and is based on Monte Carlo simulations at 10,000 runs.

3.7 Expected sensitivity to detect trends

For a proper estimate of sensitivity, a pilot study should be carried out. It depends very much on the sampling strategy, choice of matrix, how well sampling follows the guidelines, whether the same laboratory is carrying out the analyses from year to year or not etc. The sensitivity will also differ between various POPs. For biota samples in general an expected sensitivity of about 10% per year would be likely at 80% power or even better for fat fish or bird eggs. For human milk the sensitivity could be expected to be better, around 5% per year, assuming relatively large pooled samples (consisting of 25 individual samples) following the guidelines in Section 4.4.

3.8 Expected trends

Concentrations of pesticides can be expected to decrease relatively fast in environmental samples directly after a ban or other measures taken to reduce discharges, often with a magnitude of about 10 – 20 % per year. Similar trends have been measured in biota from terrestrial, freshwater and marine environments (Bignert *et al.,* 1998 a, b, c). That is, if a source disappears, the bio-available amount of hazardous persistent substances decreases much faster than what may be expected from their estimates half-times. From a statistical

point of view, this will enhance the possibilities to detect changes due to measures taken to reduce discharges, at least for persistent pesticides. For POPs like PCB or others that are found in many different products in the techno-sphere the decrease would probably be lower, say 5-10 % per year. For estimates on the possibilities to detect decreases in environmental levels of the Stockholm Convention POPs see table 3.1.

Table 3.1
Would it be possible to detect efficient measures to decrease discharges to the environment for the POPs listed in the Stockholm convention, assuming an appropriate sampling design, a monitoring period of ten years and a power of 80%?

Matrix	**Pesticides**	**Other POPs**
Biota	probably yes	probably close
Human milk	probably yes	probably yes
Air	probably yes	probably yes

3.9 Evaluation of results

GIS (geographic information system) and modelling will inevitably play a great role in the interpretation and evaluation of the results for spatial distribution and exposure etc. It has to be stressed though, that the reliability of such an evaluation will depend on the validation with real data from the environment and will become poor if the number of samples is too low. For time-series analyses a robust method proposed by Nicholson *et al.* (1995) has been used during recent years for several assessments of monitoring data within OSPAR, HELCOM and AMAP. This method supplemented with a non-parametric trend test and an efficient outlier test could form a basic package to evaluate temporal trends.

3.10 Examples of statistical treatment and graphical presentation

One of the main purposes of the monitoring programme is to detect trends. Examples of methods to detect trends could be simple log-linear regression analyses. The slope of the line describes the yearly change in percent. A slope of 5 % implies that the concentration is halved in 14 years whereas 10 % corresponds to a similar reduction in 7 years and 2 % in 35 years.

The regression analysis presupposes, among other things, that the regression line gives a good description of the trend. The leverage effect of points in the end of the line is also a well known fact. An exaggerated slope, caused 'by chance' by a single or a few points in the end of the line, increases the risk of a false significant result when no real trend exist. A non-parametric alternative to the regression analysis is the Mann-Kendall trend test (Gilbert, 1987, Helsel and Hirsch,1995, Swertz,1995). This test has generally lower power than the regression analysis and does not take differences in magnitude of the concentrations into account, it only counts the number of consecutive years where the concentration increases or decreases compared with the year before. If the regression analysis yields a significant result but not the Mann-Kendall test, the explanation could be either that the latter test has lower power or that the influence of endpoints in the time-series has become unwarrantable great on the slope. Hence, the eights line reports Kendall's '**τ**', and the corresponding p-value. The Kendall's '**τ**' ranges from 0 to 1 like the traditional correlation coefficient ‘r’ but will generally be lower. ‘Strong’ linear correlations of

0.9 or above correspond to τ-values of about 0.7 or above (Helsel and Hirsch, 1995, p. 212). This test has been recommended for use in water quality monitoring programmes with annual samples, in an evaluation comparing several other trend tests (Loftis *et al.*,1989).

In order to describe non-linear trend components in the development over time some kind of smoothed line could be applied. The smoother used in the example (Fig 3.3) is a simple 3-point running mean smoother fitted to the annual geometric mean values. In cases where the regression line is badly fitted the smoothed line may offer a more appropriate description. The significance of this line is tested by means of an ANOVA (Analysis of Variance) where the variance explained by the smoother and by the regression line is compared with the total variance. This procedure is used at assessments at ICES and is described by Nicholson *et al.*, 1995, see the smoothed line in the HCB-plot in the example (Fig 3.3).

Observations too far from the regression line considering from what could be expected from the residual variance around the line is subjected to special concern. These deviations may be caused by an atypical occurrence of something in the physical environment, a changed pollution load or errors in the sampling or analytical procedure. The procedure to detect suspected outliers in this example is described by Hoaglin and Welsch (1978). It makes use of the *leverage coefficients* and the *standardised residuals*. The standardised residuals are tested against a $t_{.05}$ distribution with n-2 degrees of freedom. When calculating the i^{th} standardised residual the current observation is left out implying that the i^{th} observation does not influence the slope nor the variance around the regression line.

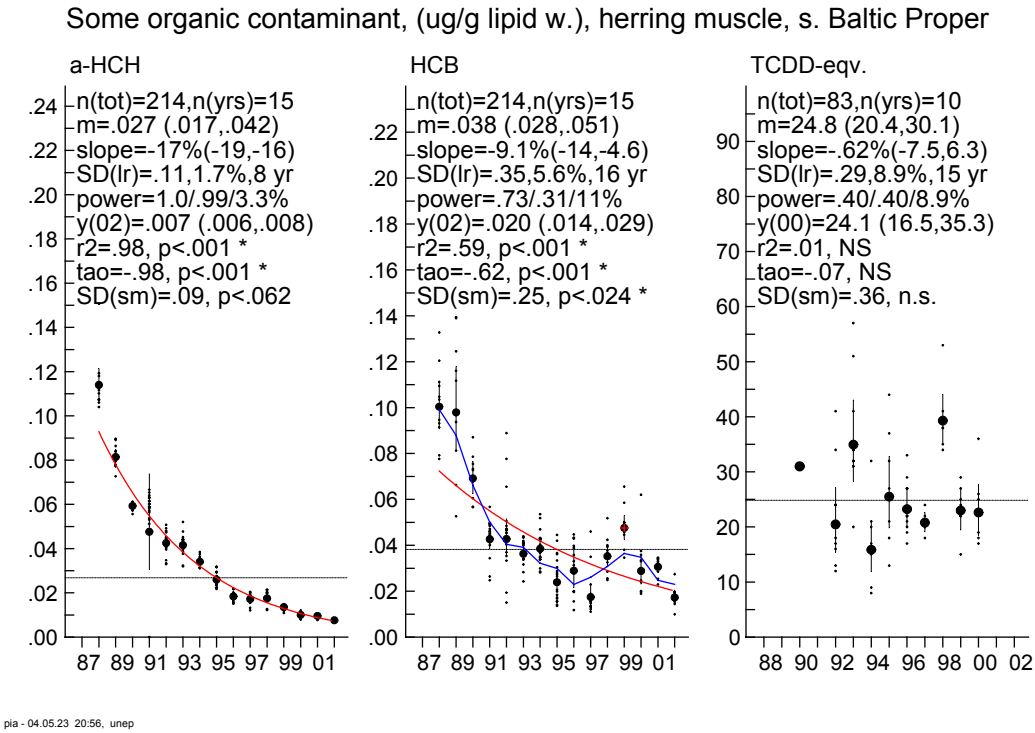

Figure 3.3 Examples of time-series; α-HCH, HCB and TCDD-equivalents (µg/g lipid weight) in herring muscle from the southern Baltic Proper. The legend to the figure is found in Table 3.2.

Table 3.2 Legend to Figure 3.3

The plots display the geometric mean concentration of each year (circles) together with the individual analyses (small dots) and the 95% confidence intervals of the geometric means. The overall geometric mean value for the time-series is depicted as a horizontal, thin line. The trend is presented by a regression line (plotted if $p < 0.05$, two-sided regression analysis). The log-linear regression lines fitted through the geometric mean concentrations follow smooth exponential functions. A smoother is applied to test for non-linear trend components. The smoothed line is plotted if $p < 0.05$. Below the header of each plot the results from several statistical calculations are reported:

n(tot)= Total number of analyses included together with the number of years (**n(yrs)=**).

m= The overall geometric mean value together with its 95% confidence interval (*N.B.* the number of degrees of freedom = n of years - 1).

slope= The slope, expressed as the yearly change in percent together with its 95% confidence interval.

sd(lr)= The square root of the residual variance around the regression line, as a measure of between-year variation, together with the *lowest detectable change* in the current time-series with a power of 80%, one-sided test, α=0.05. The last figure is the estimated *number of years* required to detect an annual change of 5% with a power of 80%, one-sided test, α=0.05.

power= The power to detect a log-linear trend in the time-series (Nicholson and Fryer, 1991). The first figure represents the power to detect an annual change of 5% with the number of years in the current time-series. The second figure is the power estimated as if the slope where 5% a year and the number of years were ten. The third figure is the *lowest detectable change* (given in percent per year) for a ten year period with the current between year variation at a power of 80%.

r^2= The coefficient of determination (r^2) together with a p-value for a two-sided test (H_0: slope = 0), i.e. a significant value is interpreted as a true change, provided that the assumptions of the regression analysis is fulfilled.

y(02)= The concentration estimated from the regression line for the last year together with a 95% confidence interval, e.g. y(02)=0.007 (0.006, 0.008) is the estimated concentration of year 2002 where the residual variance around the regression line is used to calculate the confidence interval. Provided that the regression line is relevant to describe the trend, the residual variance might be more appropriate than the within-year variance in this respect.

tao= The Kendall's '**τ**' as a result from the non-parametric Mann-Kendal trend test, and the corresponding p-value.

sd(sm)= The square root of the residual variance around the smoothed line. The significance of this line could be tested by means of an Analysis of Variance. The p-value is reported for this test. A significant result will indicate a non-linear trend component.

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4 SAMPLING AND SAMPLING PREPARATION METHODOLOGY

The main focus of a global programme that would support the effectiveness evaluation of the Stockholm Convention should be on environmental background concentrations in media with a high potential for comparability. Following this concept the March 2003 POPs GMP workshop recommended that air, bivalves, biota and humans be considered first in a POPs GMP. However, there may be cases when countries or regions choose to monitor POPs in other media (e.g. water, soil, sediments) to identify or to follow levels of POPs in hot spots. Most of the present guidance would apply also to those media, but specific considerations would be needed e.g. for sampling. Some general considerations that pertain to all the GMP matrices are discussed below.

All sampling should follow established methodological guidelines, which should be agreed to before the start of any programme activity in a region. If possible, samples in all programmes should be numbered in the same way. Sampling should always include field or trip blanks and duplicate samples.

Sample frequency and timing should be harmonized between matrices as much as possible. As a rule samples should be taken at least annually and during the same period every year. For some matrices where seasonal influences would be less important e.g. human breast milk, the sampling frequency and duration might be different. For the statistical analysis of the levels it would be preferable to take many samples frequently from one location rather than to take a few samples from many different locations. Further guidance on number of samples is given in Chapter 3.

Sample banking should be considered for all samples. Sample banking is an expensive and resource intensive activity that needs to be sustainable in a long time perspective. However, if properly managed it may yield important insights into exposures over time for e.g. new POPs and may also be used for retrospective studies. Sample banking should preferably be undertaken on a regional basis with a mechanism to enable cost sharing between participating countries.

4.1 Air

4.1.1 Experimental design

4.1.1.1 Sampling sites

When fully developed, the GMP may contain in each region (i.e. continental scale) 3 to 5 stations with active high-volume sampling, so as to gather information on baseline concentrations, trends and regional to global transport of POPs. Some of these may be sited on islands or at continental margins to gain an insight into transcontinental transport between regions. Others may be located centrally so as to obtain information on time trends of regional sources. The sites need to be sufficiently remote from urban centres and industrial and other sources of POPs as to reflect concentrations typical of a large area around the site (at least 100 km radius). Requirements for such a site include the availability of meteorological observations, the ability to perform back-trajectory analysis and station personnel who could be trained in the sampling techniques. In North America, Europe and the Arctic, some stations already exist as part of the Integrated Atmospheric Deposition Network (IADN), Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) and Arctic Monitoring and Assessment Programme (AMAP) programmes and would be used for the GMP. In other regions, use should be made of existing air quality monitoring sites that meet the appropriate site selection criteria, such as those operated by members of the World Meteorological Organization (WMO) under the Global Atmosphere Watch (GAW) programme.

Two types of measurements of a full range of POPs are envisioned in each region: (i) cumulative sampling for 1 to 2 days every week or two weeks by active high volume sampling (~1 m^3/min flow rate) at a super-sites with each sample separated into particulate and gaseous and (ii) continuous cumulative passive (diffusive) sampling for 3 to 4 months using passive samplers deployed at a large number of sites including the super-sites.

4.1.1.2 Siting considerations

In order to gain insight into the spatial variation of concentrations and time trends within the regions, the active sampling would be supplemented by an appropriate number of passive sampling sites. Whereas annually-averaged passive sampling is considered essential, quarterly resolved (3-month mean) sampling would aid understanding of seasonal variability in transport and time trends, such as may result from monsoon periods or other seasonal phenomena and is therefore recommended. Prior to their full implementation within the GMP, the passive air samplers chosen should be evaluated in a phased approach involving first a pilot study and then full implementation. The pilot study phase would address performance of the passive samplers in terms of key performance criteria to be determined in the experimental design (e.g. quantitative interpretability, ability to work under different climatic conditions, ability to sample POPs in both the gas-phase and the particulate phase).

The combination of a number of long-term active sampling sites supplemented by a larger number of passive sampling sites will yield a cost-effective programme with flexibility to address a variety of issues. Regional availability of laboratories and consideration of sources and air transport pathways will influence the spatial configuration and density of the network.

It is important to encourage co-operation between countries within regions and consultation with POPs modellers to ensure that the best sites are selected and that observational practices are standardized. Available facilities at which other atmospheric composition measurements are made should be used whenever possible.

In summary, the GMP should contain a number of active sampling sites per region that, to the extent possible, are co-located with other measurements of atmospheric composition and meteorological variables (e.g. WMO/GAW stations). Day-long samples may be taken every 1 to 2 weeks but more frequent sampling is desirable. A passive sampling network may be established in each region after a successful pilot study phase. It should include the active sampling sites. An annual passive sample from each station would be considered a minimum, while 3 to 4 samples cumulative passive samples per year is recommended.

All sites should fulfil the following criteria:

1. *Regional representativity*: A location free of local influences of POPs and other pollution sources such that air sampled is representative of a region at least 10 km in radius of the site.
2. *Minimal meso-scale meteorological circulation influences*: Free of *strong* systematic diurnal variations in local circulation imposed by topography (e.g. up-slope/down slope mountain winds; coastal land breeze/lake breeze circulation).
3. *Long term stability*: In many aspects including infrastructure, institutional commitment, land development in the surrounding area.
4. *Ancillary measurements*: For the super-sites, other atmospheric composition measurements and meteorological wind speed, temperature and humidity and a measure of boundary layer stability. For the passive sites, meteorological wind speed, temperature and humidity.
5. *Appropriate infrastructure and utilities:* Electrical power, accessibility, buildings, platforms, towers and roads.

4.1.1.3 Characterization of transport to the sites

Measurements of POPs need to be understood in terms of the processes responsible for the observed air concentration at the site. To do this, an understanding of local (meso-scale) as well as large (synoptic) scale transport pathways to the site is required. This is achieved through local meteorological measurements to characterize meso-scale influences as well as use of Lagrangian or Eulerian transport models to reconstruct the large scale transport pathways to the site.

A common transport pathway analysis tool that can facilitate the detection and interpretation of trends in POPs air concentrations is based on air-parcel back-trajectory analysis. In this approach, the transport path of air to a site during sampling is reconstructed from observed wind fields. There are various methodologies that have been applied to improve trend detection ranging from trajectory sector analysis to cluster analysis. In the latter, discriminate analysis is utilized to identify the main groups of trajectory pathways to a site (Moody *et al.*, 1998). This can be also be done for samples that fall in various percentile ranges of the trajectory distribution. Another approach that utilizes trajectories to identify sources and "preferred transport pathways" is potential source contribution function analysis (PSCF) pioneered for POPs by Hsu *et al.* (2003a and b). In this approach, upwind areas in a grid placed over the map are identified that are most frequently occupied by points in a 3 to 5 days

back trajectory for high versus low percentile trajectories. Insight into upwind sources and trends in air transported from those regions that is gained from the above analyses is much more effective in addressing policy questions than simple time-series analysis of observations.

Several models of regional and global scale POPs transport in the environment, including the atmosphere, exist (Chapter 4 of the RBA/PTS Global Report, UNEP, 2003). They simulate the large scale spatial and temporal distribution of a POPs compound including the processes of direct emissions to the atmosphere, transport and dispersion on winds, chemical transformation in the atmosphere, and air-surface exchange. These models are either coarsely resolved box models (Breivik and Wania, 2002, MacLeod *et al*., 2001, Wania *et al*., 1999) or meteorology-based models with high spatial and temporal resolution (e.g. Koziol and Pudykiewicz, 2001, Semeena and Lammel, 2003, Hansen *et al.,* 2004). In either case the size of the model domain ranges from regional to global. These models can be useful in network design and can be evaluated using POPs observations. The data together with the models are used to support the "evaluation of the effectiveness of measures taken to fulfil the Stockholm Convention".

4.1.2 Sample matrices

Air is an important matrix because it has a very short response time to changes in atmospheric emission and is a relatively well-mixed environmental medium. It is also an entry point into food chains and a global transport medium. Air data are required to validate atmospheric POPs transport models. Some sampling networks exist. As mentioned above, active and passive samplers can be combined, offering an opportunity to create a cost-effective programme. In both active and passive sampling, POPs in particulate matter and/or the gas phase are filtered from air, separated, concentrated on a filter media and extracted into a small amount of organic solvent for subsequent chemical analysis of POPs.

4.1.3 Sampling and sample handling

Air sampling requires the following capacities: (1) active and passive air samplers, (2) trained station personnel to operate and maintain the high-volume samplers, (3) meticulous preparation of clean sampling media in the laboratories performing the extraction procedures and chemical analysis. Sampling methods and QA/QC procedures should, as far as possible, be adopted from existing air monitoring programmes for POPs, but they will need to be adapted to and validated for the specific conditions, concentration levels and temperature at the sampling sites.

4.1.3.1 High volume sampling

High volume samplers should have a size-selective inlet for collecting only those particles smaller than 10 micrometers diameter. Sampling should take place using techniques practiced by routine long term monitoring networks in temperate areas (e.g. Fellin *et al.,* 1996; Environment Canada, 1994) and sub-tropical to tropical regions (e.g. Japanese Environment Ministry and National Institute of Environmental Studies). These groups recommend the technique of separating particles from gases using the combination of glass fibre filters from particles in series with two gas absorbants. The nature of the absorbants used need to be

matched to the needs of the regional monitoring programme. Several possibilities exist which are favoured for long term measurements and should be selected by experienced experts planning a regional study:

- 2 PUF plugs recognizing that some volatile chemicals (e.g. chlorobenzenes) will not be trapped efficiently. In this case, keep sample times short (e.g. especially when it is warm).
- PUF/XAD combination generally extracting and analyzing both media together.
- PUF followed by active carbon fibre felt disks.

Two absorbants are necessary to check periodically for breakthrough losses and to avoid substantive loses entailed for some semi-volatiles (e.g. HCB) especially in tropical areas.

Samples would be taken for 1 to 2 days once every week or two weeks. Every fourth sample should include a field blank. This is a set of filter and absorbants that are treated exactly as the samples including placement in the sampler except no air is drawn through them. The method detection limit (MDL) is often determined by the background amounts on these blanks rather than the analytical chemistry detection limit.

Filters and absorbents are pre-treated prior to sampling according to a methodology similar to that described in Fellin *et al*. (1996). Samples should be put into the sampling head using environment and handling practices that are free of contamination and volatilization losses. Many POPs are semi-volatile and may evaporate from sampling media if they are warmed appreciably above ambient temperatures. After sampling, samples and field blanks are extracted in the appropriate solvent (e.g. hexane and dichloromethane are common) by placing them in a Soxhlet extractor with 450 ml solvent and reduced in volume down to approximately 20 ml (e.g. see Fellin *et al*., 1996). These extracts are then split into two by placing in pre-weighed pre-cleaned vials sealed and one half shipped to the laboratory and the other half archived. This archive is extremely important to recover from accidental sample loss in the subsequent shipping and analysis at the laboratory. Also it allows samples to be reanalyzed years later when analytical techniques have improved and there is new information to be gained.

4.1.3.2 Passive sampling

Passive sampling of atmospheric gases has undergone considerable technological development in the past decade. It has matured to the state that it has been useful for surveys of ambient levels of gases in urban to regional environments (GAW, 1997). This was demonstrated in a recent multi-national study of ambient sulphur dioxide, ozone and ammonia concentrations throughout Asia, Africa and South America (Carmichael *et al*., 2003) performed under the GAW Urban and Regional Meteorology Experiment (GURME). Although the focus was on these three inorganic gases, the principle of passive gas sampling equally applies to other gases such as NO_2 and POPs. This has been demonstrated in a study done in Malaysia in which SO_2 and NO_2 were monitored (Ayers *et al*, 2000). There is an active research community that is concentrating on the development (Shoeib and Harner, 2002; Wania *et al*., 2003) and application of passive sampling to POPs. Specifically, passive air samplers have been used to map the spatial variability of POPs on a continental scale in North America (Shen *et al*., 2004, Shen *et al*., submitted) and Europe (Jaward *et al*., 2004 a, b), as well as along regional gradients (Harner *et al*., submitted; Pozo *et al*., submitted).

Carmichael *et al.* (2003) summarize the principle of passive sampling which apply to the many types of passive samplers reported in the literature. The word diffusive sampler is more specific for these samplers and is more commonly used today. A diffusive sampler has been defined by the European Committee for Standardization as: "A device that is capable of taking samples of gases or vapours from the atmosphere at a rate controlled by a physical process such as gaseous diffusion through a static air layer or a porous material and/or permeation through a membrane, but which does not involve active movement of air through the device". The gas molecules are transported by molecular diffusion, which is a function of air temperature and pressure. A net flux into the sampler is accomplished by placing an efficient sorbent for the target gas behind the barrier. The driving force is the difference between the ambient concentration and the concentration at the sorbent, which should be negligible, compared to the ambient concentration. The average net flux of pollutant through the sampler is obtained from analysis of the sorbent. The resistance of the barrier, as well as the time-weighted average ambient concentration, can be calculated using Fick's first law of diffusion.

A large number of different diffusive samplers for use in outdoor air have been developed since Palmes and Gunnison (1973) published a description of the first sampler. Several of them are today commercially available. The quality of the results from these samplers has varied widely and the technology has therefore occasionally suffered from a bad reputation. The GAW/GURME study of Carmichael et al. (2003) utilized diffusive samplers developed at the IVL (Swedish Environmental Research Institute) (Ferm and Rodhe, 1997). The IVL samplers are of badge type, 10 mm long and 20 mm internal diameter. A membrane is mounted at the inlet to prevent wind-induced turbulent diffusion. The membrane is protected from mechanical damage by a stainless steel mesh. The SO_2 and NO_2 samplers have been compared to active sampling within a routine network (Ferm and Svanberg, 1998).

Passive air samplers for POPs typically rely on a sorbent with a high capacity for POPs, such as polyurethane foam (PUF) or styrene/divinylbenzene-co-polymer resin (e.g. XAD-2). For example, Shoeib and Harner (2002) use PUF disks (approximately 14 cm diameter, 1.35 cm thick), whereas Wania *et al.* (2003) employ XAD-2 resin filled into a stainless steel mesh cylinder. The sorbent is typically housed in protective stainless steel chambers, which can either be shaped like a dome (Shoeib and Harner, 2002) or a cylinder (Wania *et al.,* 2003). Such shelters protect the sorbent from direct deposition of large particles, sunlight, and precipitation and help to diminish the wind speed effect on the sampling rate.

In order to avoid adsorption artefacts, diffusive samplers for POPs do not employ diffusion membranes which are typically used in samplers intended for volatile species as discussed above. Wind tunnel experiments measuring the uptake rate over the wind speed range 5 to 15 m/s showed that the shelter employed in the XAD-based passive sampler dampens the movement of air close to the sorbent sufficiently, to assure that molecular diffusion is controlling the rate of uptake (Wania *et al.,* 2003). Similarly, the orientation of the upper and lower domes of the PUF disk sampler dampens variable and perhaps high outdoor winds to a lower and more constant value within the chamber that is typically less than 1 m/s (Shoeib and Harner, 2002). Bertoni *et al*. (2001) have shown that the effect on mass transfer is minimal over this range. PUF disks in dome-shaped housings collect approximately 3 m^3 air per day and sample mainly the gas phase (Shoeib and Harner, 2002). This is equivalent to approximately 300 m^3 air for a 3 month integration period which is sufficiently large for detecting most target chemicals.

The XAD-based sampler in a cylindrical housing has a lower sampling rate of approximately 0.5 m^3 air per day (Wania *et al*., 2003), implying that year-long sampling is required to collect sufficiently large air volumes for the detection of many POPs in air. A more precise measure of the air volume sampled may be achieved by spiking the sorbent prior to exposure with known quantities of "depuration compounds". These are isotope labelled chemicals or native compounds that do not exist in the atmosphere and cover a wide range of volatility (assessed based on their vapour pressure and/or octanol-air partition coefficient, K_{OA}). The loss of depuration compounds over the sampling period is used to calculate the effective air sample volume (Pozo *et al.,* submitted). The air concentration is then calculated based on this air volume and the amount of chemical collected over the sampling period.

To assure that the results from diffusion samplers can be interpreted quantitatively in terms of volumetric air concentrations, it is imperative that equilibrium of a POPs between the sorbent and the atmospheric gas phase is not approached. This is particularly relevant for the more volatile POPs. If sampling is conducted at high temperatures at which the equilibrium is shifted to the atmospheric gas phase, the capacity of the sampling sorbents is greatly lowered. Shen *et al*. (2002) have measured the sorptive capacity of XAD-2 for some of the more volatile POPs as a function of temperature and concluded that the amount used in the XAD-based passive samplers is sufficiently large to prevent the approach to equilibrium even during deployment periods of several years.

Prior to use, the sorbents such as the PUF disks and XAD-2 resin, are pre-cleaned by sequential soxhlet extraction using a combination of polar and non-polar solvents (e.g. acetone:hexane and/or acetone followed by hexane). Samples are stored in solvent-rinsed and gas-tight glass jars or metal or teflon containers prior to and after deployment. Samples are extracted using the same techniques as for active air samples described above. Similarly, analysis of extracts proceeds following procedures outlined in Chapter 5.

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4.2 Bivalves

4.2.1 Bivalve molluscs as biological monitors

Biological monitors provide a mean for regular monitoring and can be used to quantify the presence of bioavailable chemicals in the environment. For this purpose, bivalve molluscs are organisms widely chosen in the marine and freshwater environments. Bivalves can filter tremendous quantities of water daily and can, therefore, accumulate pollutants in their tissues to a concentration of 1,000 to 10,000 times that of surrounding waters. The rationale behind the "Mussel Watch" approach has been extensively discussed (e.g. Phillips, 1980; 1985; Phillips and Rainbow, 1993; de Kock and Kramer, 1994; O'Connor *et al*., 1994; International Mussel Watch Committee, 1995) since the introduction of the idea in the 1970s (Goldberg, 1975). The following list of attributes of bivalve molluscs as biological monitors has been adopted from the final report for the International Mussel Watch Project (International Mussel Watch Committee, 1995; Sericano 2000):

- A correlation exists between the pollutant content in the organism and the average pollutant concentration in the surrounding habitat; contaminant concentration factors of many-fold over seawater concentrations are common.
- Bivalves are cosmopolitan, minimizing the inherent problems that arise when comparing data from markedly different species; this issue will be more important in tropical areas.
- Bivalves have a reasonably high tolerance to many types of pollution and can exist in habitats contaminated within much of the known range of pollution.
- Bivalves are sedentary and better representative of the study area than mobile species.
- Bivalves are often abundant in relatively stable populations that can be sampled repeatedly throughout the study region.
- Many species are sufficiently long-lived to allow the sampling of more than one year-class, if desired.
- Bivalves are often of a reasonable size, providing adequate tissue for analysis.
- Bivalves are easy to sample and hardy enough to survive in the laboratory, allowing defecation before analysis, if desired, and laboratory studies of pollutant uptake.
- Several bivalve species tolerate a range of salinity and other environmental conditions, making them hardy enough to be transplanted to other areas for experimentation.
- Bivalves are relatively metabolically passive to most contaminants and do not alter the chemical after uptake; uptake by the organism provides an assessment of bioavailability from environmental compartments.
- Bivalves are commercially valuable seafood and a measure of chemical contamination is of public health interest.

In addition, bivalve molluscs are able to withstand the natural stress factors present in a tidal zone (e.g. predation pressure, exposure to the atmosphere, desiccation, changes in temperature, oxygen concentration, and nutrient supply), provide integrated information of

ambient concentrations, and possess a simple, consistent relationship between external and internal concentrations of the targeted chemicals (de Kock and Kramer, 1994).

4.2.2 Experimental design

4.2.2.1 Sampling sites

Sites are the smallest geographic unit sampled. Within each site, three independent samples (stations) should be taken. These station samples are homogenized and either kept as three separated samples or pooled to provide one sample per site. When new sites are established, the three stations should be analyzed individually to know the concentration variability among samples. The intent of compositing three stations per site is to take known inter-station variability into account with each analysis.

Offshore sub tidal sites should be no larger than 300 m radius circles with the centre being the given latitude and longitude for that site. Within this 300 m radius, the three stations per sites should be collected. Shoreline inter tidal sites are defined as 100 m linear distance along a tidal horizon to either side of the site centre (local conditions may restrict this distance to less than 100 m).

4.2.2.2 Site selection criteria

Sites selected for study might represent a broad range of environmental conditions of coastal waters and a wide spectrum of contaminant loading. Site selection criteria must include the following:

- Each site must have indigenous bivalves available for collection.
- Bivalves must be present in sufficient quantities so that they will not be totally removed or significantly depleted by sampling, commercial harvest, or burial.
- Bivalves must be of appropriate population maturity and size so as to be suitable for follow-up sampling during the long-term course of a monitoring programme.
- The site should be outside the zone of initial mixing or dilution of a point source or specific disposal site.
- The site should be located so as to integrate contaminant accumulation from nearby or surrounding areas.

4.2.2.3 Background sites

A true background or control location, one that has not been affected by human activities, may be difficult to find because of the widespread distribution of man-made contaminants in the environment. Carefully chosen areas where human disturbance is perceived to be minimal can, however, provide samples that may be considered background samples. These background samples must be collected near the time and place of the sample of interest to demonstrate whether the levels of contaminants encountered at a given location are truly different from the norm or not. The collection and analysis of background samples under the same conditions as the samples of interest allows for a valid scientific comparison of

suspected contaminated samples with samples containing the analytes of interest at below detectable concentrations or acceptably low levels. The frequency of the analysis of background or control samples should be equivalent to that of a blank (e.g. one per batch of 15-20 samples). The following principles apply in selecting a background or control site (Keith, 1992):

- Should be upwind or upstream of the sampling site.
- Control samples should be collected first, when possible, to avoid contamination from the sample site.
- Travel between background or control location and sampling areas should be minimized to reduce the potential of contamination caused by people, equipment, and/or vehicles.

When a suitable local background or control site cannot be found, an area control site located in the same area (e.g. bay) as the sampling site but not physically close to it will provide the needed background information.

4.2.2.4 Site relocation of sampling site

Relocation or abandonment of established bivalve sampling sites may be necessary if the site selection criteria cannot be met or if one or more of the following circumstances pertain.

- Bivalve populations are not longer present.
- A construction project or dredging activity precludes sampling.
- Collection of bivalves is logistically impossible or would endanger the field personnel.
- Permission to sample a site or gain access to a site is denied by landowner or a leaseholder.

If the field team determines that a relocation of a sampling site is required, a decision must be made as to whether the new location is considered a minor relocation of the site or whether the new site is significantly different and should be considered a newly established site.

4.2.2.5 Site documentation

The location of bivalve sampling sites should be accurately determined and documented so that samples collected in subsequent sampling years originate from the same population of bivalves. Therefore, each site should be described with the following information: latitude, longitude, written descriptions of how to reach each site, plotted locations on official charts, and photographs.

4.2.3 Sample matrices

4.2.3.1 Choice of species

Bivalves have been extensively used to assess the concentrations of POPs in both marine and freshwater systems. While mussels and oysters are suitable biological monitors, no single bivalve species can be recommended worldwide. The green mussel, *Perna viridis*, seems to

be an excellent candidate for the monitoring of POPs in coastal waters because of its widespread distribution and their well-studied ecology and feeding habits. In areas where the green mussels are not present, other species of the genus *Perna* or *Mytilus* can be used. Oyster of the genus *Crassostrea* are also proven biological monitors, and they can be used in locations were mussels are absent. In freshwater environment, the Asian clam (*Corbicula fluminea*) has been successfully used in monitoring studies. In any case, the final decision regarding which species is best for the monitoring programme will depend on the availability of bivalves and accessibility to the sampling locations.

4.2.3.1.1 Transplanted bivalves

Transplanted or "caged" bivalves can be successfully used to monitor environmental levels of POPs in areas lacking indigenous bivalves if deployed *in-situ* for a period of time of at least 60 to 90 days. An advantage of using bivalves obtained from other areas and deployed into the area to be studied is that they may be uniform in size and have similar environmental history. The problem of lack of abundance often encountered when sampling resident individuals is also overcome. On the other hand, the loss of transplanted bivalves during the study is one of the greatest disadvantages.

4.2.3.2 Factors affecting accumulation of POPs and data comparison

Although the "Mussel Watch" concept is a straightforward procedure, there are several factors that might affect the accumulation of POPs in bivalve molluscs or complicate the comparison of data. For example, physiological parameters, differences in species availability, and environmental variations are important factors that need to be considered for a successful sampling programme.

4.2.3.2.1 Physiological parameters

Bivalve molluscs are highly dependent on season in terms of their basic physiology. Knowing how the changes in some physiological parameters in bivalves affect the accumulation of POPs in their tissue is important in order to produce meaningful and comparable data.

4.2.3.2.1.1 Lipid contents

The high lipid solubility of POPs facilitates the partition into the lipid tissue of aquatic organisms. Thus, factors that affect the lipid level in organisms can affect the concentration of lipophilic POPs in their body tissues. Several reports have demonstrated a seasonal accumulation of POPs in body tissues in response to an increase in lipid contents (e.g. Ferreira *et al*., 1990; Ferreira and Vale, 1998; Chen *et al*., 2002). Accumulation of POPs is favoured in winter when the lipid content in bivalves is higher and it is generally lower in warmer months after the reproductive phase. Winter would normally be the preferred time for sampling of bivalves in temperate and cold waters, while for tropical waters it is recommended to sample before the reproductive phase. The normalization of POP concentrations to lipid content might help to reduce the variability observed among samples with significantly different lipid levels. Therefore, it may always be advisable to report POP concentrations on dry weight basis together with ancillary parameters such as water and lipid

contents. When supporting information is given, results can be converted to a common weight database and compared to other data sets. The readers should be aware, however, that comparisons of data from different studies are difficult and must be exercised with caution.

4.2.3.2.1.2 Age and body size

Bivalve molluscs have a reasonably long life span and can be found in a wide range of sizes and age. The size of an organism is dependent on the availability of food providing the energy needed for the organism to form body tissues and to endure adverse environmental conditions. Salinity is also important for growth, in particular in brackish water systems. Differences in growth rates lead to differences in the sizes in organisms of comparable age, and this, in turn, might show differences in POP concentrations. Since there are reports that smaller individuals might accumulate POPs differently compared to larger animals (e.g. Ferreira and Vale, 1998), it is important, in long term, repetitive sampling to collect individuals within a pre-established size window, usually mature adults, to minimize the effects of different bioconcentration potentials.

4.2.3.2.1.3 Reproductive stage

Spawning is also considered to have a strong effect on the body concentrations of POPs in bivalves (Ellis *et al.*, 1993). POPs are released at the time that lipid-rich eggs and sperm are released. Because the spawning process is related to ambient temperature, it is expected that sampling during winter would minimize the influence of the reproductive phase on the body load of POPs. In temperate regions, however, mild winter conditions might prematurely onset the process of spawning in bivalves. In sub-tropical and tropical areas, where organisms are reported to spawn more than once a year, this is further complicated by a decrease in the synchronization of spawning (Clarke, 1987).

4.2.3.2.1.4 Differences in species availability

Latitude plays a significant role in the distribution of different species of bivalve molluscs available for sampling in monitoring programmes covering large geographical areas from tropical to subtropical to temperate regions. During the Initial Implementation Phase of the International Mussel Watch Programme, for example, the collection of over 25 different species of mussels, clams, and oyster were necessary to cover 76 locations in 20 countries along the east and west coasts of Central and South America, including Mexico and the Caribbean (Sericano *et al*., 1995). Although the collection of different species of bivalves might complicate the comparison of analytical results, the co-existence of some of these species at the same location can assist in the decision of whether or not it is appropriate to compare their POP concentrations or the limitations of such comparisons. In general, POP concentrations in different species of bivalves exposed to the same environmental concentrations are within a factor of four or less (O'Connor, 1991; Sericano, *et al*., 1995). The sampling of co-existing species must be exercised when possible to understand how species differences might affect comparisons and interpretation of POP concentration data.

4.2.3.2.1.5 Environmental variations

The use of bivalve molluscs in monitoring studies are based on the general assumption that tissue concentrations are correlated to ambient concentrations (e.g. water and food levels).

Although this assumption is generally true for bivalves as demonstrated by laboratory experiments (e.g. Pruell *et al.*, 1987; Sericano 1993) and field (e.g. Sericano 1993), this correlation is susceptible to environmental variables such as location relative to tide or water depth, substrate type, turbidity, salinity, wave energy, temperature and food available. Bivalves, for example, can detect ambient suspended food particles which induce bivalves to open and increase their filtration rates which, in turn, affect the exchange of POPs with the surrounding environment (Higgins, 1980; Sprung and Rose, 1988). Filtering rate, and hence bio-concentration potential, in bivalve species either increases with a rise in temperature from 8 to 25 ˚C or presents a temperature optimum range of 12.5 - 15 ˚C with a marked decline on either side of the optimum (Fisher et al., 1993). Similarly, collecting bivalve molluscs at the same time of the year, for instance in winter, can minimize biological activities triggered by temperature (e.g. spawning) that may affect POP concentrations. Adjusting sampling activities to minimize the effects that some of these conditions might have on the accumulation of POPs can be done by careful planning.

4.2.4 Sampling and sample handling

4.2.4.1 Sampling and sampling frequency

Sampling procedures, locations, equipment, and sample preservation and handling requirements are to be specified in a sampling plan. The procedures describing how the sampling operations are actually performed in the field should be specified.

A field Quality Assurance/Quality Control (QA/QC) programme must be established to ensure that the samples collected are uncontaminated and sampling procedures are properly documented. The general sampling criteria include the sampling of mature organisms from areas beyond the zone of initial dilution or suspected point-source discharge of pollutants. Preferably, bivalves should be collected from natural substrates (e.g. rocks, reef, sand, or mud) to avoid any potential contamination from artificial structures (e.g. pilings and navigation aids). If bivalves are only present attached to an artificial structure, the sample can be collected and the type of structure should be recorded in the sampling logbook.

Bivalves in inter tidal or shallow sub tidal sites can be collected by hand, with a small scraper, with tongs or using a small hand-held dredge. Sampling in deeper waters can be collected from a boat by using a larger dredge or by diving. All bivalves collected should be handled with polyethylene gloves and inspected to ensure that the shells are intact and unbroken and that specimens are alive and meet the size requirements. Personnel involved in sampling activities should have clear written instruction as to avoid sample contamination.

Winter weather conditions have perhaps the greatest adverse influence on the field sampling. In long term, repetitive sampling programmes, an acceptable sampling window (e.g. one week either side of the designated sampling day) should be established. This would provide the needed flexibility to complete the sampling activities without compromising the comparability of data.

4.2.4.2 Quality control and control samples

For all samples and data acquired during field sampling, the team leader is fully responsible for collection, processing, preservation, labelling, and onboard storage. Emphasis should be

placed on accurate positioning of the sample site, immediate processing and assignment of distinctive and unambiguous sample identification number/code, proper recording of all required information, and storage of samples and data in a safe manner. The team leader must insure that the quality, quantity (i.e. volume) and number of all samples taken are satisfactory, that the necessary information has been recorded correctly, and that sample and data handling and storage is completed promptly and accurately.

The team leader should follow routine Chain-of-Custody procedures for all samples and data; personally supervising and being responsible for their storage and transfer at all steps from the sampling team to head of the processing facility. Every transfer of samples or original data should be accompanied by a transfer form, annotating the number and nature of the samples or data, and should be signed by both the recipient and the transferring agent.

Quality control samples, typically trip blanks and field duplicates, should be introduced into the sampling process to monitor the performance of this activity. At least one trip blank and one field duplicate should be collected during each sampling activity. Enough volume for at least one sample should be collected to allow the laboratory to prepare one matrix spike and either one matrix duplicate or one matrix spike duplicate per analytical batch in order to assure data quality. Brief descriptions for each of these samples follow:

- *Trip Blank:* The trip blank, an empty container exposed to the site conditions, is used to verify that contamination was not introduced during sampling and transport activities. The trip blank is handled and analyzed in the same manner as the samples.
- *Field Duplicate*: A field duplicate sample is collected during field activities. The field duplicates are treated as independent samples during laboratory processes of preparation and analysis. Analysis of field duplicate samples is used to assess variability introduced by the sampling process and sample matrix homogeneity.

4.2.4.3 Sample treatment in the field

As samples are collected, bivalves should be scrubbed free of mud and debris using pure bristle brushes and water from the collecting site, separated and labelled according to the station and replicate. An effort should be made to retain organisms in the same size range for sampling so that organisms pooled for analysis at a site as well as replicates are of similar age and maturity. A minimum of 20 organisms should be pooled per sample to minimize the variability among individuals. When sampling, it is important to keep in mind the amount of tissue required for the analytical laboratory to complete the analyses and to process the required QA/QC samples (e.g. duplicate, matrix spike, and matrix spike duplicate). A minimum of 150-200 grams of wet tissue per pooled sample is desirable for chemical analysis. In many cases, more than 20 individuals might be needed to collect this amount. Samples should be stored in ice chests until the day's sampling is complete. At that time they should be transferred to ice chests for shipment or transportation to the processing facility. To avoid contamination, bivalves should not be opened in the field.

4.2.4.4 Sample transport

Bivalves should be wrapped in pre-cleaned (e.g. pre-combusted at 400 ˚C for 4 hours or rinsed with analytical grade solvents) aluminium foil, packed in plastic bags by location, and shipped dry, preferentially on frozen packs of ice substitute (e.g. Blue ice Brand or similar),

to the processing facility at the end of the sampling day. Mussels, for example, can survive in dry conditions for 10–14 days at temperature varying between 10 and 20 ˚C and longer at lower temperatures (Sukhotin *et al.*, 2003). If regular ice is used, bivalves should not become in contact with melted ice to avoid opening and either contamination or death of the organisms. Accumulation of water inside the ice chests should be avoided.

4.2.4.5 Sample treatment in the laboratory

Samples should, when practical, be processed the same day they are collected. Bivalves, free of mud and debris, should be shucked on pre-cleaned or combusted aluminium foil using a clean knife, the tissue collected into a pre-cleaned jar with a Teflon-lined screw cap seal and kept frozen until analysis. Each jar constitutes a unique sample and should be individually labelled with a distinctive and unambiguous sample identification number or code, the location descriptor, date, and species collected.

4.2.4.6 Sample storage

Tissue samples should be stored in pre-cleaned jars with a Teflon-lined screw cap seals at -20 ˚C in the dark until analysis. Initially, these samples should be stored as collected and not homogenized until analysis. At this point samples should be homogenized and divided into sub-samples.

4.2.4.7 Sample banking

After the analyses have been completed, the remaining homogenized tissue samples should be stored to permit retrospective analyses for the purpose of determining environmental trends, conducting inter-laboratory exercises and analyses using new and innovative analytical techniques, and providing valuable baseline data that is currently limited. Preferentially, samples should be kept in Nalgene wide-mouth cryogenic vials inside large cryogenic storage vessels filled with liquid nitrogen. These containers should be kept at -20 ˚C. Alternatively, samples can be stored in pre-cleaned jars with a Teflon-lined screw cap seals kept at -20 ˚C.

4.2.4.8 Expected cost for sampling

Low sampling costs and only minor logistical problems are posed by sampling bivalve molluscs from habitats that are easily accessed from land (e.g. coastal rocky formations, inter tidal areas). Sampling deeper water or less accessible locations (e.g. rocky formation on islands, reefs), however, pose major difficulties that can only be overcome using boats which can substantially increase sampling costs. With the exception of boat-related equipment and expenses, the tools needed for bivalve sampling (e.g. coolers, jars, gloves, oyster knifes) are inexpensive or moderately expensive. Sampling in deeper water or more isolated habitats requires a boat, related safety equipment, a boat trailer, and a vehicle capable of safely towing the boat. In any case, analytical costs will dominate over sampling costs.

4.2.4.9 Logistic considerations

The proper accomplishment of this activity should not be overlooked since it might compromise the accomplishment of laboratory analyses. Factors to be considered in planning the schedule and logistics for field sampling include the following:

- *Tidal periods and ranges.* Minus tides are generally necessary for bivalve collection.
- *Coastal surf conditions.* This is a major safety consideration. Even with extreme minus tide, large swell or waves can still inundate a site and make access to the sampling location difficult.
- *Weather.* Major storm systems can completely halt sampling operations, especially for locations on the open coast. This will cause a major delay unless sampling operations can be switched to non-affected areas. Local conditions such as morning fog and strong winds have to be considered when planning boat operations.
- *Boat launch facilities*. The location and accessibility of boat launch facilities need to be considered in boat operation schedules.
- *Dry ice availability*. Dry ice may not be available in some areas to preserve the processed (i.e. shucked) samples. In this case, the field team needs to expedite transportation of samples to the processing facility. Live bivalves can be safely transported dry and on ice packs in ice chests. Regular ice can be used avoiding any accumulation of water inside the ice chests.
- *Private property access.* Sufficient time might be needed to acquire any necessary permission and/or permits to gain access to private or government property.
- *Day light access.* This will need to be considered when planning sampling activities for sites located at the base of cliffs, on bridges or piling (safety considerations).

4.2.4.10 Links to other programmes

It is important that all POP data produced by local studies be comparable to previous environmental monitoring data produced for the area or to data being produced by ongoing monitoring programmes. “Mussel Watch” programmes have been established in many parts of the world as bio-monitoring activities for chemical contaminants in the marine environment and they can be used for comparison purposes.

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4.3 Other Biota

4.3.1 Introduction

The experts attending the GMP workshop in May 2003 stated in their report that it is important that the GMP include wildlife species, representative of the aquatic or terrestrial environments, as a matrix in the GMP in support of Article 16 of the Stockholm Convention. The wildlife matrices selected were fish, bird's eggs, marine mammals and bivalves. Since bivalves are covered in a separate section (4.2), this section will deal with fish, bird's eggs and marine mammals. A range of possible matrices were considered, mainly based on the following criteria:

- Widespread occurrence
- Site fidelity of individuals
- Well studied in terms of ecology and trophic level
- Known to be bio-accumulators
- Easily sampled

This issue of criteria regarding bio-indicator (or matrix) selection was also discussed at the STAP/GEF Workshop (2004) on the use of bio-indicators, biomarkers and analytical methods for the analysis of POPs in developing countries (10-12 December 2003, Tsukuba, Japan). The consensus was that, based on the assessment of various criteria, bivalves (and specifically *Perna* species), would be best suited for monitoring in aquatic habitats. Other aquatic bio-indicators considered were marine mammals, fish and squid. Terrestrially, only humans and birds were considered. The discussions in Japan, however, were meant to help developing countries select matrices and technologies relevant to their needs and conditions, which are different from the aim of the GMP. The GMP has the aim of supporting the effectiveness evaluation of the Stockholm Convention, rather than serving country specific needs. There is however, no obstacle to merging GMP activities with other initiatives or existing programmes where these are convenient and compatible to both, which was also expressed in the linkage discussions and reports of both the GMP 2003 and the STAP/GEF workshops.

In this section therefore, the identified wildlife species matrices of fish, marine mammals and birds (one of which needs to be selected on a regional basis) will be dealt with in an integrated manner where possible. It should be noted however, that for fish and birds, a freshwater implication is also warranted, especially if landlocked countries or systems are being dealt with. Additional material regarding the matrices can be found in Landis and Yu (1995), Moriarty (1999), Schuurman and Markert (1998) and Newman (2001).

The number of possible scenarios is therefore quite large, when dealing with three matrices in marine, estuarine, freshwater and terrestrial ecosystems. In some cases, some additional guidance or protocols may need to be developed to deal with particular conditions.

4.3.2 Motivation for selection of biotic indicators

4.3.2.1 Marine mammals as matrix

One of the major concerns during the INC process of the Stockholm Convention was that of the situation of marine mammals. The high trophic level that most of the mammals have in marine systems is well known. They also tend to have rather long life spans, and some can migrate considerable distances. They can be found in all oceans and seas, and even in some estuaries and rivers. They are endothermic animals as are humans, and could therefore be considered as good sentinels regarding human exposure and risks, although clear links have yet to be established. Most species of whales and dolphins are wide ranging, and could therefore be considered as oceanic indicators, while seals and other land associated mammals could be more representative of the more restricted areas where they feed and breed. The longevity of these animals also integrates life-long exposure, and necessarily ambient levels. Many are, however, top-predators and can therefore accumulate and transport significant amounts of POPs. Marine mammals also have high metabolic conversion rates of pollutants, and the concentrations in them may therefore not reflect the true ambient POPs levels, nor therefore sensitively reflect temporal trends. Although quite some work has been done on polar bears, consideration could also be given to other mammals that might more accurately reflect temporal trends.

Since sampling marine mammals is complicated, expensive and laden with ethical, legal (including international conventions) and conservation issues, it is recommended that, for the current purpose of the GMP, only data from existing programmes, such as those under AMAP be considered. These programmes already generate data that seem sufficient for the GMP objective of trend monitoring, in the areas under their mandates.

One of the drawbacks of using established marine mammal programmes is that there are few of these, and these do not cover the tropic and southern oceans, where many of the mammals occur. In these areas, samples of opportunity, samples from expeditions, as well as linkages with other projects that could generate samples for POPs analysis should be taken for analysis and or archival purposes. However, since much needed data can be generated from these long-living mammals, efforts should be made to collect these samples on a global level. At a later stage, the design and incorporation of a GMP programme, based on a comprehensive review of data from the tropics, southern oceans and Antarctica, should be considered as a long-term priority.

4.3.2.2 Fish as matrix

Fish is a well-known sample matrix, and many articles have been published on this topic. Most fish are relatively short-lived (when compared with mammals), and, also due to their physiology, more representative of ambient levels in water and their food items. Programmes in the Baltic and the North Sea have shown the advantages and applicability of using fish (mainly herring) as indicators of levels and trends. Again however, few or none such monitoring programmes exist in tropical and southern oceans, and most data have been derived from expeditions and surveys.

For many land-locked countries, freshwater fish, together with bivalves, probably represent the best indicators of aquatic concentrations of POPs (also due to their relative ease of sampling). Note should be taken that many countries in arid areas also have scarce water

resources, increasing the urgency of monitoring trends of POPs in these sensitive and valuable systems. Many of these systems are cyclical in nature (drought / rain season dependant), and the contribution of other sources of pollution potentially is so great (such as eutrophication), that selection of sites and species will need careful consideration. It might indeed be the case that due to other types of pollution and impact, no stable populations of fish and or bivalves will be present.

Consideration could be given in this regard to large natural landlocked wetland systems (in arid regions) that could be used as stable trend monitor sites, because of their isolated and semi-pristine nature (regarding POPs), such as the Okavango in Botswana, and Lake Chad in Chad. These remote locations might also be good sites monitoring of POPs in other matrices such as air.

4.3.2.3 Bird's eggs as matrix

As with the marine mammals, endothermic birds are also good accumulators of POPs, and therefore for trend monitoring as well. The more than 9000 bird species in the world offers ample opportunity for sampling, although there are some drawbacks that needs consideration. Many species (almost 15 %) are endangered, and many are so sparsely distributed, that egg sampling remains elusive or not viable for GMP requirements.

Bird species are also sedentary, migratory, or vagrant (opportunistic movements), and therefore requiring careful selection. The behaviour of birds are often closely related to their food items, habitat structure and other environmental requirement, and this adds to the interpretation power of the data that can be generated from egg analysis. Avian biology is also fairly well understood, and, combined with the high level of public knowledge and concern about this group of animals, it adds to their appeal as an indicator group for the GMP.

One additional measure of the impact of POPs is the effect of some of them on eggshell thickness. Collecting bird's eggs could therefore, if enough data have been collected, result in a database of levels of POPs in eggs associated with available egg measurements.

4.3.3 Criteria for species selection

In general, no species that is rare or endangered should be selected for monitoring. If specific sensitivity to, or impact from POPs is suspected on rare or endangered species, then this should be dealt with through a targeted project outside the GMP, and the results fed into the GMP.

The species selected should:

- have a wide geographic distribution
- be fairly common
- be readily collectable
- have been shown to bio-accumulate POPs
- be large enough to be sampled
- provide a large enough sample in the case of bird's eggs
- allow enough individuals to be collected over a short period of time
- have available, acceptable and tested humane and legal collection methods

The species selection has to be based on good knowledge of distribution and migration, food preferences, breeding activity, seasonal activity, stress conditions, population size and sex distribution, as well as other biological knowledge that may be available. The timing of sample collection will to a great extent depend on the biology and movement of the species. It is therefore important to have a biologist on the team, who can advise on selection, as well as assist during fieldwork.

If the area is poorly known regarding concentrations of POPs and biology of the species in question, it may be necessary to collect more than one species. Comparably cheap POPs analysis such as DDT may then be performed to select the species with the highest BCF. Some sampling is non-destructive, and the animals can be marked for later identification, possible recapture and re-sampling. This data should be part of the reporting, and should also be kept centrally (see Chapter 6).

All legal requirements, such as local and CITES permits must be obtained, thereby including the authorities of both the country of collection, and the country where the analysis will be conducted. It should also be noted that ethical approval will in many cases be required, adding to the administration of the projects, and can result in considerable delays.

4.3.3.1 Marine mammals

The marine mammal species for existing programmes have already been selected, and these should not be changed. For new areas however, species selection will need to follow as closely as possible, the taxonomic and trophic relationship with those that are already being sampled. In the absence of polar bears in the Antarctic, the relatively common leopard seal could be used, if such a need should arise. This animal is predatory upon other seals and penguins, and seems to be fairly common and adaptable to changing conditions, and also occurs all the way around Antarctica. In many seal species individuals may be wide ranging. Younger animals which would have had less chance of being contaminated during such distant excursions may thus preferably be sampled.

4.3.3.2 Fish

Again, only species close in taxonomy and trophic levels to those that are being used elsewhere (or that have a good data base available), should be considered for selection. There are more than 30 000 species of fish, so selection should be done at the regional level, but with good relevance and reference to what has been done before, and selections based on what has been shown to work well elsewhere. In Africa for instance, catfish (*Clarias garipinus*) would be a suitable species, since much work has been done on this fish, with regards to pollution studies (Osibanjo *et al*., 2002). If taxonomic related fish are not available, then species of similar size and food preferences should be considered. Again, the support of a taxonomist is required.

- Where possible, fish high in the food chain (e.g. bass, sea bass, cod, greenling, angry rockfish, and black porgy), or fish with a high fat content (such as bottom-dwelling sharks and rays), should be sampled.
- The timing of sampling plays a significant role, as seasonal variation in fat content can be considerable, also in freshwater species.

- Migration is important to consider, not only for marine fish, but also for freshwater species, that can migrate up or down river according to flooding and breeding patterns.
- Commercial fish should be high on the list of species that can be selected, but care should be taken when species experience dramatic population changes due to over exploitation.
- Ecological keystone species is another criterion that can be considered when selecting a species, as long as most of the other criteria are also being met.

4.3.3.3 Bird's eggs

Terns and gulls are obvious candidates for the programme, since they have already been extensively studied. Herons and raptors also have a fairly good database. Other criteria to consider regarding birds are:

- Species should lay eggs that are large enough.
- Enough eggs can be collected in relatively short period of time.
- Egg sampling from double-clutching species would reduce the impact on the population (sampling from the first clutch).
- Disturbance of the colony cannot always be prevented but should be minimised to reduce predation, radiation from the sun, cold, prolonged absence of parents from the nest, and trampling.

One of the constraints when selecting migratory birds is that they breed only at one end of the migration route. Migratory birds will integrate POPs along the route through feeding, and would therefore give good, large geographic range data, but this data is not easily interpretable as to source and temporal trends. Here, consideration could be given to terns as a group of species, since they occur worldwide, have both sedentary and migratory species, and many breed in colonies all over the world.

Raptorial birds have been used with good success, but the eggs are not always easily collectable, in many cases the breeding occurs over large areas, and, seasonal food availability could limit the number of breeding attempts, especially in arid areas.

As mentioned before, additional measures of the temporal effects of some POPs are evident on the egg morphology. Obtaining this information should be done as a standard procedure during collection, and kept centrally for future use, as part of the archives and sample banking for the GMP.

4.3.4 Guidelines for site selection

In general it can be stated that, as is also the case for air and bivalves, sites or regions of sampling should have the following characteristics:

- Lack of local anthropogenic sources of POPs. The distance of the closest source will depend on the natural range of the species and habitat type.
- Sites or regions should be representative of a much larger area or coastline or ocean, also taking prevailing winds and currents into account.
- The species should be indigenous to that region or site.

- The site or region should be a general feeding and or breeding site for the selected species, or alternatively, be located on the normal migration route or stopover site of that specific species.

An additional concern in many tropical countries is the fairly general use of insecticides in areas other than arable lands. Locust control, mosquito control, pest bird control, tsetse fly control, and a variety of other legal and illegal uses may contribute towards localised, but irregular (except in the case of malaria control) pollution episodes. This should be taken into account, although it will be difficult to monitor this type of activity over the intervening non-sampling periods.

In all cases a proper site characterisation will have to be done. Where possible this should overlap with other GMP activities, such as air monitoring, where meteorological information will be available. If not, consideration should be given to obtain meteorological data from the closest station.

Some countries have, or are considering instituting Long Term Ecological Research (LTER) sites (e.g. the South African Environmental Observation Network), which could also be considered as a site for GMP sampling, since the additional data could be used in the future for modelling purposes.

4.3.4.1 Marine mammals

Three types of marine mammals, based on their habitat, could be considered. Pelagic species roam the open ocean (e.g. many whales and larger dolphins). Benthic species are more closely associated with the continental shelves, and the coastal species are those that are associated with coasts and ice floes. Coastal species, such as seals and walruses, need to come on land or ice for breeding. Although regular sampling of large whales would likely provide very good integrated temporal trend information (although with a lag time associated with the longevity), even non-destructive sampling would be quite costly. Relying on strandings of whales and dolphins does not meet the criteria of the GMP for various reasons, mainly the biased selection. The scientific catches of whales that are allowed should be utilised to its fullest extend. Samples obtained from hunting should be used as far as possible where this applies. Conservation requirements and public perceptions that accompany the monitoring of marine mammals are complex, and great care should be taken if designing a study that would require additional sampling.

Note should be taken that seals may be wide ranging. Individuals can visit harbours or polluted estuaries, and return to relatively pristine areas, or *vice versa*. Timing of collection for seal samples would be during the summer season.

4.3.4.2 Fish

Migration will play a significant role in site selection. Again, biological knowledge of breeding and migration will be required to select sites or regions. For freshwater fish, where possible, late summer to early fall fish would be the recommended, taking reproductive status into account. It should be collected either in the upper catchments, or in large impoundments, lakes or wetlands, upstream from known anthropogenic sources of pollution. The role of

melting water from mountains as a confounding factor for concentrations of POPs should be considered.

4.3.4.3 Bird's eggs

Colonially breeding birds are suitable for collection. For non-marine birds, colonially breeding birds are mainly those associated with wetlands such as herons, spoonbills, cormorants and ibises. These locations should be stable. They may be located within conservation or protected areas. Care should be taken as it can happen that entire colonies suddenly move, due to a variety of reasons. The timing of egg collection would be during the breeding cycle, preferably collecting freshly laid eggs. At least 12 eggs pooled from different nests within the same colony are recommended to be taken.

4.3.5 Criteria for tissue selection

4.3.5.1 Marine mammals

Non-destructive sampling of blubber from marine mammals should be the norm where possible, or else, blubber samples from existing programmes or from legal hunting should be considered. Ethical considerations are important, as hunting of seals is allowed in some countries, but may not be internationally acceptable to some donors. Biopsy samples, taken from captured mammals such as polar bears are quite small, and may restrict the range of POPs that can be measured. Due to the nature of the sample sources, individual analysis of each sample is preferred.

Additional concerns regarding sampling of marine mammals are the great variation in POP levels between species, within species, within a population, between genders, with age etc. In addition, general health as well as nutritional and reproductive status is known to influence the concentration. This means that in order to determine temporal trends for the GMP, a large number of individuals would be sampled and the sampling procedure must be standardised with regard to e.g. size, age, gender, time of year, nutritional and reproductive status. For more information, consult the AMAP reports (AMAP 1998).

4.3.5.2 Fish

Depending on various factors such as size and fat content, either whole fish, fillet or fat can be sampled. Smaller species can be homogenated whole and extracted, while larger species will need either filleting for muscle tissue, or dissection for fatty tissue. EPA and other protocols on sampling and analysis are available on the web. In general, and for the purpose of the GMP, replicate composite samples of adult fish of the same size and sex should be done. At least 12 fish per pooled sample per site is recommended (see Chapter 3). Field duplicates and field blanks should be included in the protocol.

4.3.5.3 Birds' eggs

Depending on the species and availability of eggs, either single or pooled samples of eggs should be taken. Consideration could be given to species that have the ability to "double clutch", i.e. to lay a second consecutive clutch, if the first clutch is lost or destroyed. At least

12 single eggs from different nests per site are recommended to be collected (see Chapter 3). Field duplicates and field blanks should be included in the protocol.

4.3.6 Sample collection, storage and transport

The criteria for sampling, storage and transport will have the same elements of sample description (collecting all pertinent information) chain of custody, sample ID and other issues in common with similar types of environmental samples. In all cases clean sample containers are fundamental. Foil needs to be pre-cleaned and, where in contact with sample, the dull side should be used.

4.3.6.1 Marine mammals

Blubber samples should be collected in clean glass jars, with Teflon-lined lids, or else lined with foil. All materials coming in contact with the sample should be cleaned with detergent and reverse osmosis water, and then rinsed with analytical grade acetone and allowed to air dry. Where possible, the sample container should be tared and weighed during dissection to obtain the fresh weight. It should be transported on wet ice or frozen during transport, and kept frozen until analysis.

4.3.6.2 Fish

If whole fish cannot be filleted or dissected directly after collection (preferable), then spines should be removed, and the whole fish individually wrapped in foil (dull side against the fish), and then placed in polythene bags. The bags should then be placed on ice, or chilled to 4°C for transport to a processing laboratory. The fish should then be processed within 48 hours of collection, or frozen until this can be done. Depending on the species it should be scaled (allowing frozen specimens to thaw partially), and then filleted using clean equipment and work surfaces, and rinsed between each specimen (EPA protocol on sampling and analysis).

4.3.6.3 Bird's eggs

As far as possible, fresh eggs should be collected (candle the eggs during collection), and all measurements taken on site. Although fresh eggs can keep for a while if kept on ice, the contents should be transferred to clean glass jars as soon as possible (with Teflon or foil lined lids), and frozen during transport. If eggs contain embryos in advanced stages of development, these should be stored and used separately. They will in general not be useful for the GMP, as metabolism of the POPs have already begun. The eggshells should also be labelled, air-dried with the membrane intact, and packaged securely. Any tools used to collect the contents should be washed with detergent, rinsed with reverse osmosis water, and rinsed with analytical grade acetone.

4.3.6.4 Voucher specimens

Where possible, voucher specimens should also be collected and deposited locally, or at established museums, to aid in taxonomic identification. With molecular technology, it is likely that species might later be split or lumped, which could confuse future comparisons.

4.3.7 References

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AMAP, 1998	http://www.amap.no
South African Environmental Observation Network	http://www.nrf.ac.za/saeon/
EPA protocol on sampling and analysis	http://www.epa.gov/waterscience/fishadvice/volume1/index.html

4.4 Human milk as a biological monitor

Human milk has been used for monitoring of human body burdens of particularly PCB and PCDD/PCDF for several decades. The idea behind most studies on chemical contamination of human milk has been to discover the infant burden of the chemicals from nursing. An important idea of human milk studies is also that this matrix reflects the contamination at a high trophic level. Thus, human milk samples reflect the intake in different regions: the extent of contamination and different consumption habits. Otherwise, hundreds of food samples of different matrices, origin and production times would have to be analysed to provide intake data. Furthermore, such studies are also used as general biological monitoring tools. Thus, human milk monitoring programs have been designed for assessing levels of environmental pollution by lipophilic substances in different areas within and between countries. Trends in levels and effectiveness of regulations have been evaluated by comparing these assessments with earlier investigations.

Few countries have systematic human milk monitoring programs that have tested considerable numbers of women over time using consistent sampling methods. Comprehensive human maternal blood monitoring with standardized protocols for specimen collection and analysis has been done in the Arctic where maternal blood, supplemented with some human milk data have been used in assessing POPs and human health (AMAP 1998, 2004). Furthermore, WHO has organised three rounds of exposure studies in 1987-1988, 1992-1993 and 2000-2001, on levels of POPs in human milk (WHO 1989, 1996, van Leeuwen and Malisch 2002, Malisch and van Leeuwen 2003). The main objectives of these studies were: 1) to produce more reliable and comparable data on concentrations of PCB, PCDD and PCDF in human milk for further improvement of health risk assessment in infants, 2) to provide an overview of exposure levels in various countries and geographical areas, 3) to determine trends in exposure levels. Nineteen European countries participated in the second round, in which concentrations of PCB, PCDD/PCDF were determined in milk samples collected in a total of 47 areas. The third round of WHO-coordinated exposure study was initiated in 2000. In order to collect data in more countries, also beyond the European region, the study was organised in collaboration with International Programme on Chemical Safety (IPCS) and WHO Global Environmental Monitoring System/Food Contamination Monitoring and Assessment (GEMS/Food). In the last round of exposure studies 18 countries participated and milk samples from 62 different areas were analysed. Historical trend data exist for PCDD/PCDF and PCB in some of these countries (e.g. Becher *et al.* 2002). For some countries a pilot study of concentrations of other POPs than PCB and PCDD/PCDF has been included in the latter study. In these studies pooled human milk samples were used. A fourth round of exposure studies is being planned by WHO European Centre for Environment and Health (WHO-ECEH), the IPCS and the GEMS/Food. The main objective of the fourth round will be to produce reliable and comparable data on levels of POPs in human milk which will serve as basis to determine time trends in exposure to POPs.

4.4.1 Objective of human milk monitoring within the GMP

The human milk monitoring within GMP will mainly aim at identifying temporal and as appropriate, spatial trends of POPs in exposure levels of humans.

In addition regional capacity building in developing countries focused to ensure a capability to detect regional trends of such chemicals in human milk will be aimed.

4.4.2 Sampling and sample preparation methodology

4.4.2.1 Sample matrices

The GMP programme will use human milk as one matrix for biological monitoring. See the proceedings of the GMP workshop for more information on the recommendation for the selection of human milk as matrix suited for temporal trend studies in GMP.

Human milk is an attractive medium because it is non invasive and relatively large volume of samples can be easily collected in a more or less standardized manner. A disadvantage of using human milk is that of a biological sample. Another disadvantage is of course that only one gender constituting a limited age group is monitored. As the main aim of GMP is to determine a temporal trend in exposure to POPs the restriction of concentrating only on a small, but well defined part of the population, can be considered to be an advantage. However, in certain areas there are social or ethical difficulties to overcome in the collection of human milk samples.

The GMP will use pooled human milk samples. The analyses of pooled human milk samples represent an easy and cost effective method for comparing POP levels between and within countries and to elucidate time trends. A disadvantage with pooling is of course that information on individual variation is missed. It may therefore be recommended that aliquots of individual samples be archived for analyses when resources and capacity are available. Additional studies can of course be implemented within countries to answer questions that are country specific.

Since some national authorities perform contaminant analyses in maternal blood samples, it would also be acceptable that maternal blood may be used within GMP. Blood sampling, however, has some ethical and hygienic negative aspects concerning AIDS and HIV. Maternal blood sampling would be part of a regional or sub regional program and should follow an established methodological guideline.

4.4.2.2 Experimental design

Under WHO, a protocol has been developed for sampling and sample preparation methodology for exposure studies of PCB and PCDD/PCDF in human milk (1987-1988, 1992-1993 and 2000-2001). However, even though time and geographic aspects were addressed in these previous WHO organised studies the design of the protocols was optimized for health risk assessment. The protocol for the fourth round of exposure studies using human milk will be finalized during spring 2004. This WHO revised protocol will be expanded with regard to substances being monitored and the number of participating countries. It will be particularly extended beyond the European region in order to support and strengthen national capabilities for the monitoring and sound management of hazardous chemicals on a global scale.

To ensure the reliability of exposure data and to improve comparability of analytical results from different laboratories, the WHO Regional Office for Europe and the WHO European Centre for Environment and Health, Bilthoven Division, have coordinated a number of inter-laboratory quality assessment studies. The fourth round on levels of PCB, PCDD and PCDF in human milk was conducted between February 1996 and April 1997. The objective was to identify laboratories, whose results could be accepted by WHO for exposure assessment studies. The final report presents the results of the study and a list of accepted laboratories for each of the studied compounds. As only the State Institute for Chemical and Veterinary Analysis of Food met all the criteria for analyses of PCDD, PCDF, dioxin-like PCB, marker PCB and fat in human milk, this laboratory was selected as reference laboratory for the third round of the WHO exposure study (WHO 2000, Malisch and van Leeuwen 2002). However, while in the third round of exposure studies WHO had all the samples analyzed at this highly qualified laboratory in Germany, in the fourth round they intend to involve regional laboratories and preclaim capacity and competence building in developing countries and the protocol will be developed accordingly. Thus, the fourth round of exposure studies organised by WHO can contribute to the effectiveness evaluation of the Stockholm Convention. Close collaboration between UNEP and WHO on this issue will be mutually beneficial.

The revised WHO protocol gives guidance on the number of samples/sampling locations and selection of donors. The existing WHO questionnaire is being amended and instructions are written on collection, storage and transportation of samples as well as on pooling procedures. It is recommended that countries participating in the GMP adapts the guidelines set in the WHO protocol and align with the above mentioned program. The issues discussed below are thoroughly addressed in the WHO protocol.

4.4.2.2.1 Number of samples/sampling location

Milk from well-defined groups of mothers living in at least two areas with different exposure levels should be collected and pooled in each country/region. The main requirements of the POPs GMP are the detection of spatial patterns and temporal trends in representative background locations, away from immediate sources, and an improved understanding of global and regional transport. Countries representing different regions, Africa, Asia and Pacific, Central and Eastern Europe, Latin America and the Caribbean, and Western Europe and North America must be included. A great variation in levels of new and old POPs must be expected. It is recommended that the regions themselves take part in suggesting and deciding which particular country and which area in the specific country that should be sampled. A goal must be that it should be possible to repeat sampling after a determined period of time (to assess time trends). Also the sampling area should be representative for a particular living condition and agricultural as well as industrial activity. Recommendations on aspects of site selection are given in the proceedings of the GMP workshop.

4.4.2.2.2 Selection criteria for mothers

There are many factors explaining the variation in concentrations of POPs found in human milk and it is important to define selection criteria for the mothers to be included in the study (Harris *et al.* 2001).

- Exposure; Sampling location/exposure situation must be described. It is also important that the mothers have been living in the particular area for some time (5 years).

- Parity; the mothers should nurse their first child and nurse only one child (multiple births excluded)
- Health; both mother and child should have apparently good health.
- Age
- Social/Economic condition

4.4.2.2.3 Questionnaire

It is recommended that the questionnaires developed for the fourth round of the WHO exposure studies are adopted (This questionnaire is still under development). Questionnaires should be filled in for all mothers.

4.4.2.2.4 Sampling and sample handling

Time post partum for sampling, time of the day, time of sampling with respect to feeding of infant etc will probably have to be compromised taking into account that tradition and way of living for mother and new born may differ very much between sampling areas. However, strict recommendations with regard to sampling must be pronounced. Under the WHO program sampling should begin when lactation is fully established after 2-4 weeks post partum and continues if possible until 2 months. Each participating country submits at least 2 samples of milk, each representing a pool of milk from at least 10 mothers (preferably more, see Chapter 3). Individual countries may of course expand the number of samples they analyze under the GMP or to pursue their own programme and country specific needs. The statistical basis of the WHO protocol is under revision. Thus, recommendations on the number of samples needed may be revised (see revised WHO protocol when available and Chapter 3 of this Guidance Document).

Pooling should be done on a volume basis by using 50 ml of collected milk from each mother. The minimum number of individual samples is 10, making a total of at least 500 ml pooled milk available for analysis. Before pooling the samples it is recommended to examine the questionnaires to exclude obvious potential outliers (e.g. smokers, mothers with extreme dietary preferences, mothers that lived less than 5 years in the area).

With regard to sample collection (use of pumps, flasks etc), sample handling (freezing or preservation by addition of potassium dichromate) and archiving, the revised WHO protocols could be followed in their entirety.

Sample handling is particularly important for obtaining homogeneous samples of human milk for analyses and to ensure sample integrity (Lovelady *et al.,* 2002). Therefore the guidelines on handling of samples as laid down in the protocol should be strictly followed. Qualified personnel must be available to undertake the sampling and training may be required.

During sampling of human milk from one mother the sample may be stored at 4 ˚C for a maximum of 72 hours. In countries where temperature control is not possible, the collection of milk samples should be done in bottles in which a tablet of potassium dichromate has been added. This method of preservation of the milk sample was applied successfully by some countries at the third round of WHO-coordinated exposure studies (van Leeuwen and Malisch, 2002; Schecter *et al.,* 2003).

When pooling samples from a number of mothers each sample must be heated to 38 ˚C and inverted gently several times to mix the cream layer. Thereafter a predetermined aliquot from each sample is pooled. The pooled sample is treated similarly and aliquots are divided into separate vials to minimize freeze-thaw cycle during analyses. The samples can be stored at -70 ˚C for an infinite length of time. When the sample is ready to analyze thaw and temper to 38 ˚C. Mix by gentle invasion and extract the entire sample. The container should be rinsed with solvents. Procedures for sample handling during storage, transport to analytical laboratory and handling by analyst etc must be developed to take into account both cross contamination by chemicals and transfer of disease between people.

4.4.2.2.5 Ethics

All human sampling must conform to national ethical guidelines

4.4.3 Transporting of samples

Shipping of samples to the selected analytical laboratory within the region/country should be done in accordance with instructions given by the responsible party.

4.4.4 References

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5 ANALYTICAL METHODOLOGY

This document will not give a detailed description of the analytical methods to be used for the analysis of POPs. It will not even prescribe the use of specific methods that have been described for this purpose, as this would delay the development and acceptance of new, improved methods. The intention is to give a general description of the analytical procedures, and to give references to how this is done in other monitoring programmes. It is, however, essential that the methods used are validated to give comparable data from all regions.

Analytical methods for the determination of POPs in environmental samples and biological tissues vary depending upon the matrix and required limit of detection. Analytical procedures are composed of the following four steps: 1) sample collection and extraction, 2) clean-up using partition and chromatographic fractionation 3) separation on gas chromatography (GC), 4) detection with selective and sensitive detectors. Since the early 1960s, POPs have been determined using gas chromatography (GC) techniques with electron capture detection (ECD), initially using packed columns. More advanced methods, such as capillary GC-ECD and GC coupled with mass spectrometry (GC-MS) have been used in more recent studies to identify the individual congeners, to improve the comparability of the analytical data from different sources and to establish a basis for the understanding of geochemical cycles and toxicological implications. In addition, effect-based methods utilizing specific binding to the Ah receptor may be used to quantify the total Toxic Equivalent from Ah-receptor binding chemicals present in a sample. The sensitivity and selectivity of these methods is not yet comparable to that of HRGC/HRMS and the methods cannot identify individual congeners, which is needed for source identification. In addition, national legislation very often specifies the application of HRMS to generate reliable results.

Based on the availability of commonly used instruments for the determination of POPs, three types of laboratories can be identified, as described in Table 5.1.

Table 5.1 Requirements for the instrumental analysis of POPs

Laboratory tier	Equipment	Infrastructure needs	Cost (USD)	Chemicals
3	Basic sample extraction and clean-up equipment, capillary GC/ECD [a]	Nitrogen/air conditioning/ power/personnel specifically trained to operate and trouble-shoot equipment problems	Instruments: $50K Lab equip: $30K Operation: $10K/year Personnel: 2 PY	Most PCB and all OCPs except toxaphene.
2	Sample extraction and clean-up equipment, capillary GC/LRMS [b]	Helium/air conditioning/ consistent power/ personnel specifically trained to operate and trouble-shoot equipment problems	Instruments: $150K Lab equip: $50K Operation: $20K/year Personnel: 3 PY	Most PCB and all OCPs; toxaphene if negative chemical ionization is available.
1	Sample extraction and clean-up equipment, capillary GC/HRMS [c]	Helium/air conditioning/ consistent power/high operational costs /personnel specifically trained to operate and trouble-shoot complicated instrumentation	Instruments: $400K Lab equip: $50K Operation: $50K/year Personnel: 5 PY	PCDD/PCDF, all PCB, all OCPs except toxaphene.

[a] GC/ECD – gas chromatography/electron capture detection
[b] GC/LRMS – gas chromatography/low resolution mass spectrometry
[c] GC/HRMS – gas chromatography/high resolution mass spectrometry

A good network within a region would contain at least one tier 1 laboratory and several tier 2 and 3 laboratories. A tier 1 lab could be responsible for the training and quality assurance work within the region if it is well trained for the analysis of POPs. If such a lab is not available in the region collaboration with labs in other region(s) is necessary.

The applications of biomarkers (endpoints of ecotoxicological tests that register an effect on a living organism) are developing fast. Presently, it is not possible to get the accuracy that is needed to detect temporal trends for POPs with biomarker methods (STAP/GEF workshop report). As these alternatives in most cases are much cheaper than the chemical analyses, the development has to be followed carefully.

5.1 Links to other programmes

Before starting new measurements, it is important to investigate if there are any other monitoring activities going on in the region. It may be global programmes, like the WHO GEMS/Food, UNEP Regional Seas Program, or national monitoring activities. Another source of information are the reports from the recent global assessment of PTSs. It is assumed that the GMP shall, at least partly, be based on existing activities, and co-operation with those is essential. This may also influence the strategy for the chemical analyses, and if the methods used in on-going projects are good enough those can be applied also for the GMP.

5.2 Analysis

Numerous methods have been published over the past 40 years on the specific analytical techniques for determination of POPs in food and environmental matrices. Laboratory standard operating procedures (SOPs) for analysis of POPs are available from agencies such as US EPA (NEMI) and Japan Environment Agency. Useful information may also be available from ICES (Techniques in Marine Environmental Sciences), OSPAR (Joint Assessment and Monitoring Program), HELCOM, International organization for Standardization, Association of Official Analytical Chemists International, and Gosstandard of the Russian Federation.

It is anticipated that improved analytical methods will be developed over the life of the GMP. The project should be structured so that these improved techniques can be adopted. There is a need to improve the accuracy and lower the costs of these analyses. Emerging procedures with low environmental impact (microscale, immunoassay, low solvent use, etc.) may become more widely available and accepted. It will be necessary to consider comparability as new methods come along. This could be achieved by analysis of archived samples and direct comparison of new and old methods. Many environmental laboratories are not currently allowed to analyze human blood and milk samples. Special training will be necessary to handle these samples, considering the danger of infectious diseases.

Table 5.2 provides general guidance for various preparation, extraction and isolation steps in the analysis of PCB and OCPs. Starting with sample preparation, the basic approach is to assure that the sample is prepared for extraction in a room that is free of significant contamination. Ideally this would involve a well ventilated lab with air pre-filtered through HEPA (HEPA Corporation) and carbon filters but any clean chemical laboratory facility should be adequate for most work on PCB and OCPs in most matrices except water, or soils and sediments from remote locations. The analysis of blank samples will disclose background interferences, and to identify the influence from the laboratory environment, a small volume of a solvent left in an open Petri dish for a couple of days will catch the compounds in the atmosphere. Memory effects in glass ware can be avoided by heating the glass to 300 ˚C over night before use.

Wet samples should not be air-dried to avoid contamination from lab air, especially in the case of PCB (Wallace *et al.,* 1996), and to avoid possible volatilization losses. Instead homogenized samples should be mixed with a drying agent such as sodium sulphate or Celite. The drying agent must be certified to be free of POPs e.g. by heating at high temperature in the case of sodium sulphate or pre-extraction (Celite).

Table 5.2 Guidance for various preparations, QA, extraction and isolation steps in the analysis of PCB and OCPs.

Matrix	Analytical steps	General procedures
Fish and shell fish.	Preparation	Select muscle or liver depending on species. For mussels and crustaceans use soft tissue. Select tissue that has not been in contact with the sample container. Homogenize using food chopper or blender. Cryo blending is useful. Mix with drying agent. Separate determination of lipid.
	QA	One blank and fish or mussel CRM every 10 samples; spike all samples with recovery surrogate standards. Bake glassware by overnight heating at 200ºC or higher.
	Extraction	Soxhlet, Accelerated Solvent Extraction, or column extraction, use acetone: hexane or dichloromethane (DCM).
	Isolation/cleanup	Remove lipid using gel permeation chromatography if possible or by repeated washing of the extract with sulphuric acid (the latter will partly destroy dieldrin). Follow with fractionation on Silica or Florisil columns.
Marine mammal blubber	Preparation	Select blubber that has not been in contact with the sample container. Blend or hand mix with drying agent. Separate determination of lipid content.
	QA	Same as fish. Use fish oil or marine mammal SRMs and LRMs.
	Isolation/cleanup	Same as for fish extracts.
Birds eggs	Preparation	Homogenize the egg content.
	QA	One blank and fish CRM every 10 samples; spike all samples with recovery surrogate standards. Bake glassware by overnight heating at 200ºC or higher.
	Extraction	Soxhlet, Accelerated Solvent Extraction, or column extraction Use acetone: hexane or DCM.
	Isolation/cleanup	Same as for fish extracts.
Air (high volume)	Extraction, QA and cleanup	Assuming that air is collected on PUF or XAD resin these would be extracted in a Soxhlet or Pressurized fluid extractor.
Semi-permeable membrane devices (SPMD)	Preparation	SPMDs would be removed from their transport cases and rinsed with pre-cleaned water to remove accumulated dust (air borne samplers) or periphyton (water samplers).
	Extraction, QA and cleanup	Assuming that the SPMD is lipid based, extraction of POPs by "dialysis" into hexane would be achieved in a large glass cylinder.
Human milk	Extraction and cleanup	Follow the new WHO guideline when available.
Human blood (AMAP method E-347-G-)	Sampling	Vacutainers, anticoagulation, centrifuge, freeze plasma
	Extraction and cleanup	Ammonium sulphate/ethanol/hexane (1/1/3), Florisil column, dichloromethane/hexane (1/3) + acetone
	Determination	GC-NCIMS
	Lipid determination	Sum of free cholesterol, triglycerides and phospholipids determined by enzymatic methods.

5.2.1 Extraction and clean-up

The appropriately prepared sample can be extracted by any one of a number of techniques. There is a need to agree on the method used in each region before starting the sampling. The main points to consider are to allow adequate time of exposure of the solvent system in the sample matrix and to limit sample handing steps, i.e. avoid filtration steps by using Soxhlet (sample in a glass thimble) or semi-automated systems (e.g. pressurized fluid extractors, EPA method 3545A). Extractions can also be accelerated by the use of ultrasonication. Cross contamination from residues left behind by high levels of POPs in other samples is a concern at this stage and equipment must be thoroughly cleaned and checked from batch to batch. Purity of extraction solvents is also a major consideration. Only high purity glass distilled solvents should be used. Internal standards should be added to the sample as early as possible in the process.

If the results are reported on a lipid weight basis, the determination of the lipid content in the sample is critical. From this aspect the choice of solvents is crucial, and has been discussed in a recent article (Jensen *et al.,* 2003). If the whole sample is not used for the extraction, the remaining part can be frozen and stored for future control analysis, or analysis of other substances. Likewise the extracts not used in the analysis can be stored, preferably in glass ampoules, at -20 ˚C.

Isolation steps can be relatively straightforward for low lipid samples such as air, soils, sediments and vegetation. Generally small Silica gel or Florisil columns (either prepared in the lab or pre-purchased) will suffice. The purpose of this step is to remove co-extractive pigments and to separate non-polar PCB (plus p,p'-DDE) from more polar POPs (HCH, most chlordanes, dieldrin/endrin). This is achieved by applying the extract in a small volume of non-polar solvent and fractionating by eluting with hexane followed by one or two other elutions of increasing polarity. Alumina is not recommended because of possible dehydrochlorination of some POPs, e.g. 4, 4'-DDT.

For high lipid samples, such as fish tissue and marine mammal blubber, a lipid removal step must be included. This can be achieved using size exclusion or gel permeation chromatography (GPC) either in automated systems, using high pressure liquid chromatography (HPLC) columns or by gravity flow columns. The advantage of GPC is that it is non-destructive while the disadvantage is a requirement for large volumes of solvent (low pressure or gravity systems) or expensive columns (HPLC). Lipid removal using sulfuric acid washing or sulfuric acid – silica columns is also effective but does result in loss of some analytes such as dieldrin.

Following fractionation on silica or Florisil final extracts are prepared in small GC vials for analysis. Addition of a recovery standard to check solvent volume is recommended at this stage. Careful evaporation is required at this step and only high purity compressed gas (usually nitrogen) should be used.

Analytical methodology for PCDD/PCDF and PCB with TEFs differs from those used for routine ortho-PCB and OCPs in requiring much lower detection limits (typically 10-100 times lower) because guideline limits in food products are in the low pg/kg range, the Provisional Tolerable Monthly Intake being 70 pg/kg body weight (Joint FAO/WHO Expert Committee on Food Additives (JEFCA), 2001). To enforce and control these low concentrations for PCDD/PCDF isotope dilution MS (^{13}C-surrogates for all PCDD/PCDF

homolog groups), enrichment on carbon to isolate planar compounds, very small final volumes (10-50 µL) for GC-HRMS quantification is used. Methodology for PCDD/PCDF, slightly modified to include the dioxin-like PCB, developed by the US EPA, is well established and validated by numerous inter-laboratory comparisons. This methodology would be recommended for use in a global monitoring program. Unlike the guidelines for PCB and OCPs, this very specific guidance for the extraction, isolation and quantification steps for PCDD/PCDF is recommended in order to be in compliance with ongoing programmes and compatible with results generated with these methods over the past 10 years.

5.2.2 Determination and detection limits

Numerous analytical approaches are available for quantifying PCB, and OCPs, as well as PCDD/PCDF by gas chromatography. As with extraction/separation steps only general guidance is required for ortho-substituted PCB and OCPs. However, a major consideration is that the laboratories will have access to modern capillary GC equipment and either electron capture or mass spectrometry detection. Some general guidance on the application of gas chromatographic analysis of ortho-substituted PCB and OCPs is provided in Table 5.3. For PCDD/PCDF and PCB with TEFs, quantification solely by isotope dilution HRMS is recommended and details can be found in SOPs (e.g. EPA method 8290A).

HRMS can also be used, of course, for determination of all ortho-substituted PCB (e.g. EPA method 1668) and OCPs as well and indeed would provide a very high level of confidence in the results compared to GC-ECD. However, use of GC-ECD is recommended because of wide availability, relatively low cost, and the substantial knowledge base that exists on the use of this technology for analysis of ortho-PCB and OCPs at low ng/g levels or higher in environmental matrices.

Table 5.3 General guidance on GC analysis and data reporting for POPs

GC detector	Analytes	Configuration	Advantages/disadvantages	Detection Limits [1]
Capillary GC – with Electron Capture Detection	All ortho-substituted PCB and all OCPs on the POPs list except toxaphene	30 or 60 m x 0.25 mm id. column with H_2 carrier gas. Dual column, non-polar (DB-1) and intermediate polarity columns (DB-5)	Similar response factors for most OCs. Good sensitivity for all POPs. Adequate for routine tasks. High potential for misidentification of some POPs due to co-eluting peaks	Examples: DDT/DDE ~ 1pg HCB ~0.5 pg
Quadrupole mass spectrometry in Electron Ionization (EI) mode.	All PCB and all OCPs on the POPs list except toxaphene	30 m x 0.25 mm i.d. low bleed columns with He carrier gas. Selected ion mode for target POPs	Newer instruments (post 1997) have adequate sensitivity for routine POPs monitoring at low pg/μL concentrations. Much less potential for mis-identification than with ECD	Examples: DDT/DDE ~ 1-10 pg HCB ~1-10 pg Dieldrin ~ 25 pg Toxaphene ~ 500 pg (as technical mixture)
Quadrupole Mass spectrometry in Electron Capture Negative Ionization (ECNIMS) mode.	Toxaphene and other highly chlorinated OCPs and PCB with > 4 chlorine atoms	30 m x 0.25 mm i.d. low bleed columns with He carrier gas. Selected ion mode for target POPs	Comparable sensitivity to ECD in SIM mode for some POPs, in ECNIMS mode. Much less potential for misidentification than with ECD.	Examples: DDT/DDE ~ 0.1 pg HCB ~0.1 pg Dieldrin ~ 1 pg Toxaphene ~ 10 pg (as technical mixture)
Ion trap mass spectrometry using MS/MS mode	All PCB, All OCPs on the POPs list	30 m x 0.25 mm i.d. low bleed columns with He carrier gas. Same columns as quadrupole MS	Comparable sensitivity to ECD in MS/MS mode for some POPs. Much less potential for mis-identification than with ECD	Examples: DDT/DDE ~ 1 pg HCB ~1 pg Dieldrin ~ 5 pg Toxaphene ~ 100 pg (as technical mixture)
High resolution magnetic sector mass spectrometry in Electron Ionization (EI) mode	PCDD/ PCDF, all PCB, all OCPs on the POPs list except toxaphene	30 m x 0.25 mm i.d. low bleed columns with He carrier gas. Selected ion mode for target POPs at 10,000 resolution	Comparable sensitivity to ECD in SIM mode. Highly reliable identification at low pg/uL levels.	Examples: DDT/DDE ~0.05 pg HCB ~0.05 pg Dieldrin ~ 0.1-0.5 pg Toxaphene ~ 10 pg (as technical mixture)

[1]The smallest amount introduced in the instrument that can be detected at S/N of ~10.

The lowest concentration at which a compound can be detected (limit of detection, LOD) is often defined as that corresponding to a signal three times the background. The lowest concentration that can quantitatively be determined (limit of quantitation, LOQ) is normally three times higher than LOD. Compounds found at levels between LOD and LOQ can be reported as present, or possibly as being present at an estimated concentration, but in the latter case the result has to be clearly marked as being below LOQ. Results below the detection limit are often reported as <LOD.

There are, however, several statistical techniques for treating censored data when the true detection limit is known, e.g. by using a robust statistic such as the median which is unaffected by small numbers reported as below LOD.

An alternative is to replace values reported as below LOD with approximated values. For example, a common method is to allocate half the value of the detection limit. In these cases, the estimated annual mean concentration will depend both on the detection limit and the value allocated to non-detected results in the data set. In general the estimate of the true mean value will be biased.

Another method use an estimate of each unknown concentration based on the empirical expected order statistic (Helsel and Hirsch, 1995). This method fits a log-linear regression of the ranked detected concentrations on rank, and then uses this relationship to predict the value of those concentrations reported as below the limit of detection (Figure 5.1).

In the analysis of complex mixtures, such as PCB, there is always a risk for coeluting peaks in the gas chromatograms, and known interferences should be reported.

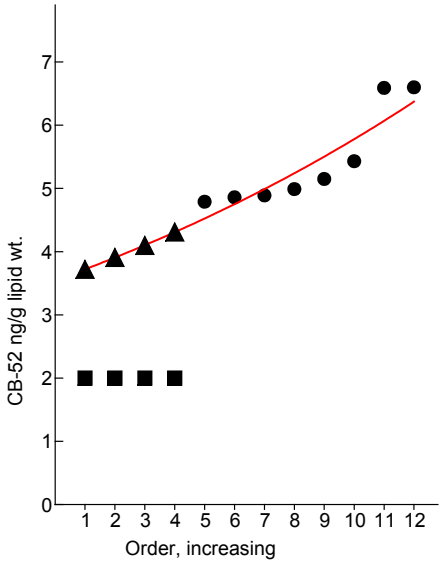

Figure 5.1 Example of substitution of concentrations reported as less than LOD, by extrapolation from regression of concentrations from the same annual sample above LOD on rank order. Log-linear regression fitted to data above LOD. Circles = concentrations above LOD, Triangles = substituted values for concentrations reported as below LOD, Squares = LOD/2 – values.

5.3 Quality control

Quality assurance/quality control (QA/QC) is a system to ensure that the data generated by a laboratory are of the highest quality possible and thereby acceptable to all parties. This section aims at providing the conceptual basis and the principles for dealing with the issues of QA/QC in the GMP. The rationale for providing such a framework rather than prescribing detailed quantitative requirements is based on the following: a) Describing analytical criteria in detail is a very comprehensive task. Different groups are dealing with this issue and often with slightly different conclusions that require much time to harmonize. The QA/QC criteria to be applied for the GMP have to be in line with internationally accepted criteria and adapted to changes such as technological developments. b) The GMP will be a dynamic process in terms of the range of concentrations of POPs and the matrices to be analyzed. The QA/QC system has to be adapted and optimized according to the actual state of the program. The aim with the GMP is to produce comparable monitoring data at a global scale. A high reproducibility is also needed to be able to detect small annual changes in concentration to verify any temporal trends in the data. It is important that also the sampling process is included in the overall QA/QC system of the programme (see Chapter 4).

5.3.1 Organisation

To achieve globally comparable data some inter-regional activities are needed. This may include support of standard material, reference material and inter-calibrations.

As was mentioned above it is anticipated that a tier 1 laboratory act as a central point in the regional network. It could then also be responsible for the regional QA/QC work and perform confirmatory analyses when necessary. This laboratory could also be given a mandate to provide guidance to the other laboratories in the region on QA/QC methods. Preferably, all laboratories should be accredited. In addition, laboratories with an appropriate QA system that can meet the pre-set criteria can participate and gradually, through capacity building activities, be supported to achieve accreditation.

All laboratories involved should be selected according to their ability to meet a set of quality criteria. Laboratories accredited for the analysis of POPs will be accepted and do not need further audits, as they are already being externally audited on a regular basis. Laboratories, having a QA/QC system, but no POPs accreditation, will be evaluated by an expert group that will identify those with sufficient quality to enter the programme and the potential to obtain accreditation within a reasonable period of time. Another key criterion for laboratory acceptance should be the ability to achieve minimal, globally accepted detection limits, accuracy and precision. Typical acceptable values for a number of QA parameters have been specified in the EU legislation.

5.3.2 Components of QA/QC procedures

Key elements in QA/QC are the use of reference materials and quality charts, participation in inter-laboratory studies, and the use of guidelines for sampling and analysis.

5.3.2.1 Reference materials

Certified reference materials (CRMs) are available for a number of POPs (see Table 5.4). The use of CRMs, a key component of QA/QC procedures, is required where available.

Table 5.4 CRMs for POPs in biota

CRM		c-C	t-C	dieldrin	PCDD/ PCDF	DDTs	HCB	mirex	PCB
SRM1974b	mussel	X	X			X			X
SRM1588a	cod liver	X		X		X	X		X
SRM1945	whale bl.	X				X	X	X	X
SRM2977	mussel	X		X		X			X
SRM2978	mussel	X	X	X		X			X
140/OC	plant			X		X			X
BCR598	cod liver	X	X	X		X	X		X
CARP-1	carp				X				X
BCR349	cod liver								X
BCR350	mackerel								X
BCR682	mussel								X
BCR718	herring								X

c-C: cis-chlordane; t-C: trans-chlordane

For a number of POPs and matrices however, CRMs are not available, and GMP will have to establish ways to make them available, either by contacting dedicated organisations, or through specific projects under the GMP programme.

The use of laboratory reference materials (LRMs) and the preparation of quality charts will be of high importance. Thus, the preparation of large batches of LRMs is recommended, either at a central level or at each participating laboratory.

5.3.2.2 Inter-laboratory studies

Proficiency tests for all the POP/matrix combinations, at least on an annual basis, are desirable. Such an annual assessment is mandatory for accredited laboratories. This could be a scheme especially organised for the GMP programme or part of existing inter-laboratory/proficiency testing schemes. However, for matrices such as human samples or air, there may be only limited possibilities. For these matrices, preference could be given to the coordination of the inter-laboratory studies under the GMP programme.

Inter-laboratory studies for POPs have been developed since the late 1970s. Some of the first studies were organised by the International Council for the Exploration of the Sea (ICES). Soon, it was observed that one-off inter-laboratory studies were of little value. These first exercises often resulted in a wide range of results, while later repetitions did not show any

improvement. Stepwise designed inter-laboratory studies were more successful. A group of experts was responsible for the design of the exercise and for scientific advice to the participants, and objectives and targets for analytical performance were identified (Nicholson, 1989; Wilson, 1979). This advice helped participants to improve their methods and to obtain better results. The first stage of such a study normally focused only on the analysis of a standard solution. Later steps were gradually made more complex: analysis of clean extract, analysis of raw extract, and analysis of real matrix. In this way the specific problems of the various steps of the analysis could be discussed. Because of the complexity of the POP analysis, this model proved to be successful. Between-laboratory standard deviations of for example PCB analysis could significantly be reduced (de Boer *et al.,* 1992, 1994, 1996). This model was also used within the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) programme (Wells *et al.,* 1997). An additional improvement of this programme was the organisation of dedicated workshops. At those workshops all analytical details were discussed, following a first exercise in which participants had often made various mistakes. The laboratories were assisted, by means of a stepwise designed study, to build up their method and reach a good comparability with other participants. This approach was for example successfully used for the analysis of toxaphene (de Boer *et al.,* 2000), and is currently being carried out for brominated flame retardants.

Proficiency tests are being organised by various national and international organisations. A series of five proficiency tests for trace metals and a number of organochlorine pesticides in food was organised in 1993 and 1994 by the Global Environmental Monitoring Scheme (GEMS) of the World Health Organization (WHO) (Weigert *et al*., 1997). These tests, which were carried out according to the international harmonized protocol for the proficiency testing of chemical analytical laboratories (Thompson and Wood, 1993a,b), showed that of the 136 participating laboratories only 41% were successful for organochlorine pesticides analysis. This indicated that care is needed in the collection of data from monitoring programmes, and also the need for further measures to improve the performance of the participating laboratories.
In addition, it is recommended that laboratories regularly share samples for analysis, e.g. one sample per batch at a monitoring laboratory could be analyzed by the central laboratory in the region.

In the absence of CRMs and inter-laboratory studies, the analytical performance should be demonstrated by regular blank analysis, spiked samples, duplicates, and confirmatory analyses as described by the International Union for Pure and Applied Chemistry (IUPAC, 2002).

5.3.2.3 Other important QA components to be reported

- Sampling protocols (e.g. method, number, size, representativity)
- Limit of detection/quantitation
- Concentrations in blanks should be reported, and if those values have been subtracted from the result this shall be clearly stated
- Recoveries
- Duplicates
- Calibration
- QA of co-factors (such as lipid, organic carbon and moisture content)
- Confirmatory tests (e.g. use of second GC column or another detection system)

5.4 References

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UNEP Regional Seas Program	http://www.unep.org/water/regseas/regseas.htm
National monitoring activities	http://www.chem.unep.ch/gmn/02_natpro.htm.
Global assessment of PTSs	http://www.chem.unep.ch/pts/default.htm
US EPA	http://www.nemi.gov
Japan Environment Agency	http://www.env.go.jp/en/topic/pops/index.html
ICES	http://www.ices.dk/env
OSPAR	http://www.ospar.org
HELCOM	http://www.helcom.fi/Monas/CombineManual2/CombineHome.htm
International organization for Standardization	http://www.iso.org
Association of Official Analytical Chemists International	http://www.aoac.org
Gosstandard	http://www.kanex-krohne.com/english/Downloadarea/gosstandard_russia.shtml
EPA method 3545A	http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3545a.pdf
EPA methodology for PCDD/F	http://www.epa.gov/SW-846/pdfs/8290a.pdf http://www.epa.gov/Region3/1668a.pdf
EPA method 8290A	http://www.epa.gov/SW-846/pdfs/8290a.pdf
EPA method 1668	http://www.epa.gov/Region3/1668a.pdf
EU legislation on QA	http://europa.eu.int/eur-lex/pri/en/oj/dat/2002/l_221/l_22120020817en00080036.pdf http://europa.eu.int/eur-lex/pri/en/oj/dat/2002/l_209/l_20920020806en00150021.pdf
Quality charts	http://www.eurachem.ul.pt/guides/EEE-RM-062rev3.pdf
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6 DATA HANDLING

The results from the GMP will be used to determine trends from monitoring of POPs globally to support the effectiveness evaluation of the Stockholm Convention. Effective data sharing among relevant bodies by consistent data communication methodology is essential to achieving this objective.

Global monitoring data may be reported using a wide variety of formats. Definitions for a standardised format will be important in order to develop a data warehouse that can be useful for the purpose of the effectiveness assessment. The use of models will be important for the understanding of environmental transports within and between regions, but this will not be further treated in this guidance document.

6.1 Data quality

Prior to being included into the database, laboratory results should have passed all the quality criteria. Therefore, data should be scrutinized by the laboratory generating them in the first place. Then the data, confidence intervals and all supporting information on QA sampling and methods should also be evaluated by a regional quality review panel. To avoid problems in the data handling it is essential that there is an agreement on which units to be used. The following units are suggested:

POPs	Air	Bivalves, biota and human milk
All except PCDD/PCDF	pg m^{-3}	ng (g lipid)$^{-1}$
PCDD/PCDF	fg m^{-3}	pg (g lipid)$^{-1}$

If data are reported on a lipid weight basis as suggested, the content of lipid (% fat) has to be reported to facilitate recalculations to a fresh weight basis as well. Also the method used for the lipid concentration should be reported.

The definitions of the limit of detection (LOD) and the limit of quantitation (LOQ) need to be harmonized. A possible method has been described by the USDA Pesticide Data Program. A system of flagging should be developed for data that are generally acceptable but do not fulfil all quality criteria, and also for those data that are between the LOD and the LOQ. Non-detects should normally be reported as less than the LOD, the value of which has to be reported (if another method is used it has to be clearly specified, see Section 5.2.2). For TEQ calculation in the case of dioxin analysis, it is strongly advised that upper bound and lower bound values be reported in keeping with the recommendations by JECFA (Joint FAO/WHO Expert Committee on Food Additives).

It is also important that the methods used for the determination of concentrations and meta data, such as lipid content, are well described. This can be included in the data base as such, or by reference to method description in other sources.

6.2 Data policy

While a proportion of the data generated under the GMP will be made available for public access soon after its generation, some of the data may be subject to a moratorium until the scientists responsible for the data have been able to publish papers covering the results. This presents a clear constraint on the general preference for early public access to scientific data, but is one that must be allowed for in the data handling policy of raw data. Furthermore, there is a need to provide recognition of data sources, acknowledging the names of the researchers and technicians conducting the sampling and analytical procedures.

In considering potential public access to data, a distinction is usually made between raw data (i.e. untreated sample measurement data) and aggregated data (i.e. data that have been subjected to forms of treatments, such as taking an average). There is often less sensitivity to publication of aggregated data as they are not as easily identifiable with specific samples or areas.

Minimum data reporting requirements need to be established to ensure consistency among the data sets between regions. These data reporting requirements should include the following: analytical measurement, with the reporting basis (e.g. lipid weight); site identification and site description; sample identification; sample characteristics; sampling method; analytical method; QA/QC assessment, and data ownership. Further details of the reporting requirements will need to be determined when the monitoring programme has been specified in greater detail.

To promote comparability among the regions, harmonized assessment tools (such as statistical methods for temporal trend evaluations) and products should be agreed. This again will need to be determined in association with the further elaboration of the monitoring programme and the associated assessment methodology.

6.3 Data flow

Data for the evaluation of the effectiveness of the Stockholm Convention will come from at least three different categories of sources. One of these is the direct supply of data from laboratories associated with the GMP. The second category is contributions from other monitoring programmes (international, regional and national). The third group would include other sources, such as individual scientists, independent institutes, industry and Non-Governmental Organisations (NGOs). A model for the information flow is shown in Figure 6.1.

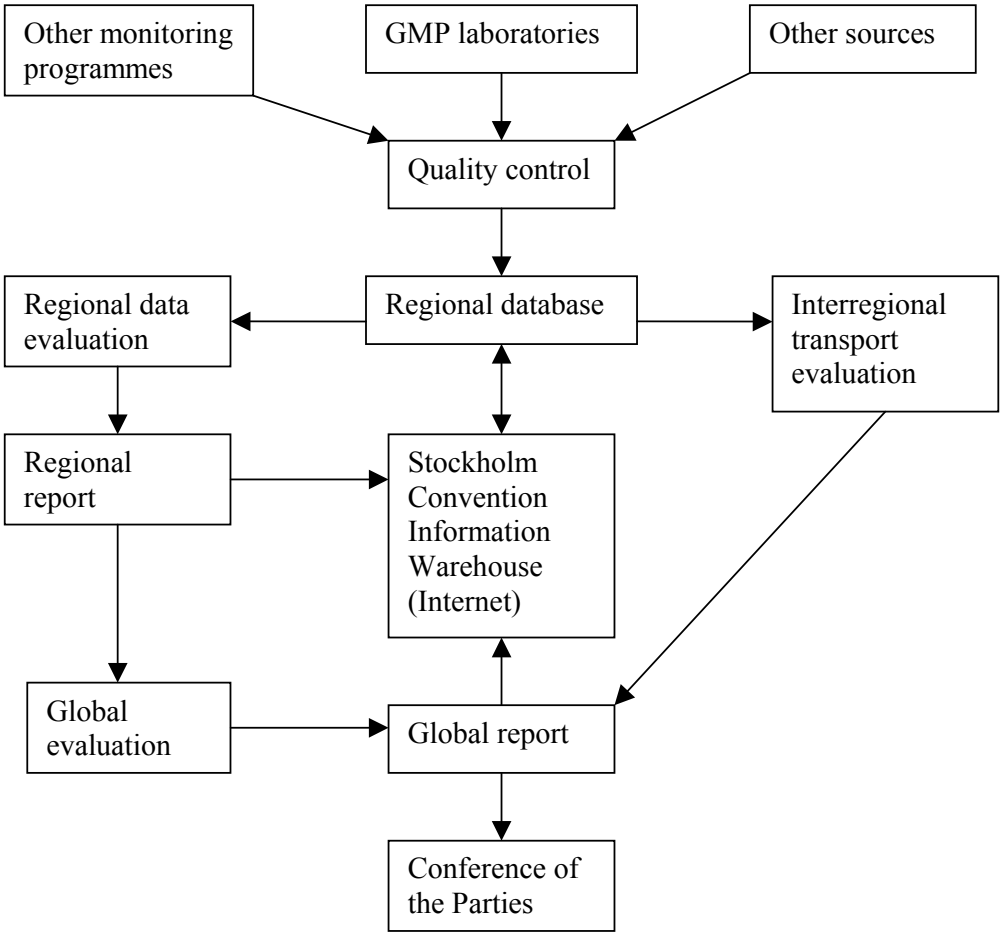

Figure 6.1 A possible model for the data flow from the GMP laboratories and other sources to the COP.

After the quality control process the data are stored at regional data centres. Data that can be made public may be open for access through the information warehouse or stored in this warehouse. Thus information can be retrieved from the warehouse independent on the physical location of the data. The warehouse could also collate other types of information on POPs, which may be useful in the evaluation. The regional data centre will support the regional evaluation process with the material. The resulting regional reports will be fed into the information warehouse, and be used for the global evaluation. In parallel there may be an interregional evaluation of environmental transport of POPs, which also will feed into the global report (or possibly into a global environmental transport report). The format of the data will depend on both source and receiving organisation, but a common format for the whole GMP would be beneficial.

6.4 Data storage

The model outlined in Figure 6.1 contains one storage facility in each region and one at the global level, the information warehouse, for the entire GMP. The latter is a collection of

aggregated data used to support the regional assessment reports, and the regional and global reports in electronic format and any other information that the COP wishes to disseminate. The purpose of this warehouse is transparency of process.

There are today a number of good examples of international data warehouses, some of which are:

- The International Council for the Exploration of the Sea (ICES) has been developing a monitoring database for more than 2 decades. ICES Environment data center has been collecting marine contaminants and biological effect data from 19 member countries and its reporting format is used for reporting data for AMAP, OSPAR and HELCOM. The reporting format and coding system are shown on the ICES website. This format is well-organised and detailed for marine samples including biota, sediment, seawater, and recently a number of biological effects. The format includes the meta data information concerning sample nature and analytical protocols.

- AMAP (Arctic Monitoring and Assessment Programme) is showing a data collection of POPs monitoring data. Although the web-based presentation is under development, example data is already presented on the website. The example data shows mean and range of measured data for each sampling point for each river.

- EMEP (Cooperative Program for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe under Convention on Long-Range Transboundary Air Pollution) also collects POPs monitoring data, however, there is no web-based presentation of the data as yet.

- UNEP GEMS/Water (Global Environmental Monitoring System/Freshwater Quality Programme) has been working on the data compilation and presentation of the monitoring data for water and food environment. UNEP GEMS/Water website has been showing monitoring data for physical/chemical pollution parameters, major and minor ions and organic contaminants, including POPs. The presentation format is somewhat simple, but covers 69 countries.

ICES could be used as a reference or guide for developing a data reporting format, since ICES includes the major meta data items especially concerning the nature of the sample and analytical protocols.

The UNEP GEMS/Water database has a great deal of data but with less information on meta data. This may be due to the fact that the major monitoring items are physical/chemical water quality parameters, which have harmonized sampling and measurement protocols nearly everywhere in the world. Environmental monitoring for POPs may require a larger variety of meta data information, so the discussion on this topic may be more important for POPs monitoring.

One problem with the way data is displayed on some of the Internet sites mentioned above is the focus on the sampling site as opposed to the sampling results. While it is critical to have information about the site where monitoring is performed, displays of data also need to include summaries of data with a chemical focus. Canada NPRI (National Pollutants Release Inventory) and USEPA TRI (Toxics Release Inventory) do this better than other sites. The

use of graphs, in addition to tables and maps would also add to the visual understanding of the data.

Analyses of POPs are expensive and many of the results produced in the GMP will be unique. It is therefore essential to make as much as possible of the data accessible to many users. There is, for example, a big need for monitoring data for development and validation of distribution and transport models. To support these other uses of the results, also the original data need to be accessible at the information warehouse.

The problems and costs to develop new data bases shall not be underestimated. Also the maintenance and updating of the bases also takes big resources. An option for the GMP would be to buy this service from already established programmes.

Recognition must be given to the diversity in regional capabilities. This should include recognition that in some regions relevant programmes and associated data handling solutions already are in place. Clear consideration must be given to how to utilize these existing activities so as to avoid duplication and take advantage of existing expertise. At least in some regions there are already programmes and activities for managing relevant data, some of which may include the GMP data. Not only is there a desire to make use of existing solutions, but also to avoid establishing new systems that might inadvertently have negative consequences for existing arrangements.

6.5 Data analysis

Monitored contaminant concentrations together with information of variance will be of value as reference values to other studies without any further analyses but in general monitoring data are typically subjected to temporal and spatial analyses but also e.g. for compliance with environmental assessments criteria. The various objectives require different techniques for analyses but also the type of data will influence the choice of e.g. statistical methods used.

The identification of trends will require that statistical evaluation be thoroughly carried out on the programme design as a whole to ensure that it is powerful enough to detect trends of interest including establishing the target accuracy of the analysis.

It should be kept in mind that the statistical power is likely to be reduced when data from more laboratories are used. Given the expected variability in results of inter-laboratory studies, it is recommended to record site-specific trends in POP concentrations based on results of single laboratories.

6.6 References

USDA Pesticide Data Program	http://www.ams.usda.gov/science/pdp/Qc10.pdf
JECFA recommendations	http://www.inchem.org/documents/jecfa/jecmono/v48je20.htm#3.2.3
ICES Environment data centre	http://www.ices.dk/env/index.htm
ICES Reporting format	http://www.ices.dk/env/repfor/index.htm
AMAP data collection	http://www.amap.no/
UNEP GEMS/Water	http://www.cciw.ca/gems/gems.html
Canada NPRI	http://www.ec.gc.ca/pdb/npri/npri_home_e.cfm
USEPA TRI	http://www.epa.gov/tri

7 ANNEX A: DRAFT STRUCTURE FOR REPORTS

Introduction

In order to assist in the elaboration of the GMP, it would be useful to consider how the final assessment reports may be structured. The drafts presented here have been prepared to assist the GCG and the RIGs while they are planning and setting up their information gathering activities. In this context they can serve as a reference tool by which managers can check whether key important information required for an assessment is being included in the planning and information gathering process. The draft structure should not however be considered the structure which will finally be developed and adopted by the GCG and the RIGs.

Background

In the absence of an existing comprehensive discussion on the structure of the reports, the draft structures outlined below are founded upon an examination of the objectives of Article 16 of the Convention and of the GMP, together with a consideration of how other initiatives have approached similar tasks. Although a number of regional and global monitoring programmes have been established to report on the presence of POPs in the environment, there is very little previous experience of POPs monitoring designed to help evaluate the effectiveness of a legally binding international agreement. The 1998 Protocol on POPs under the Convention on Long-range Transboundary Air Pollution (which entered into force in October 2003) (UNECE 1998) contains in Article 10 a requirement to review the sufficiency and effectiveness of the obligations taking into account the effects of the deposition of POPs. However arrangements to undertake this work are still being formulated.

POPs have been included in a number of monitoring programmes established to support international pollution prevention agreements, such as the periodic assessments for the Baltic Sea under the 1992 Helsinki Convention (e.g. HELCOM 1996) and the Joint Assessment and Monitoring Programme under the 1992 Oslo and Paris Conventions for the Protection of the Marine Environment of the North-East Atlantic (OSPAR 2000). Monitoring to support action is also envisaged in a number of UNEP's Regional Seas Monitoring and Assessment Programmes and Action Plans with a varying degree of implementation. Examples include the Barcelona Convention's Mediterranean Action Plan; and, the Convention for the Protection and Development of the Marine Environment in the Wider Caribbean Region. Resulting assessments are published under the UNEP Regional Seas Reports and Studies Series. A North American monitoring and assessment programme which will include the present 12 Stockholm Annex POPs is being developed in Canada, Mexico and the United States (CEC 2002).

In addition, a number of global and regional assessments of the state of the environment (but not linked to pollution control agreements) have included POPs. Examples include: the various marine environment assessments undertaken by Group of Experts for the Scientific Assessment of Marine Pollution (e.g. GESAMP 2001); and the assessments undertaken for the circumpolar Arctic by the Arctic Monitoring and Assessment Programme (AMAP 2002-4), and for Europe (EEA 1998). Other programmes have included a regional or global survey

of the levels of certain POPs in particular media. Examples are the Global International Waters Assessment (GIWA 2000); the International Mussel Watch Project (e.g. Farrington and Trip, 1995; O'Connor, 1998; and Tanabe, 2000); and, surveys of certain organochlorines (including PCB, PCDD and PCDF) in food and in human milk (GEMS/FOOD 1997, GEMS/FOOD 1998, van Leeuwen and Malisch. 2002).

Proposed planning process

It is envisaged that when the Conference of the Parties has approved the arrangements for the GMP, the GCG in consultation with the RIGs would produce a supplement to the Guidance Document which would elaborate detailed guidance for the preparation of the regional and global assessment reports. It would include an annotated structure for each type of report. A draft is provided in this section.

DRAFT STRUCTURE OF REGIONAL REPORTS

1. INTRODUCTION

- The objectives of Article 16 of the Convention and of the GMP.

2. ORGANISATION

The over-arching organisational strategy for the GMP and for the assessment and reporting process.

- UNEP sponsored preparatory workshops, and inter-net based consultations and communications;
- Establishment, and responsibilities of the GCG and of the RIGs;
- Global agreement on a basic framework to provide comparable information;
- Regionally developed and executed implementation plans based upon the global framework;
- The Regions - their boundaries and reasons for their selection; and,
- Sub-regional arrangements (e.g. identification and rationale for any sub-regions that may have been created).

2.1 Information gathering strategy. Brief description of the process and decisions taken to decide what information would be needed (regardless of whether or not there are pre-existing sources of that information), focussing upon the formation of the sampling matrix.

2.2 Strategy for gathering new information: Explanation in the context of the sampling matrix regarding media, site selection, sampling frequency, and agreed protocols to preserve sample integrity (e.g. quality control, transport, storage, and sample banking).

- Air
- Biota
  - Bivalves
  - Bird eggs
- Supplementary biota (fish and marine mammals)
- Human tissue (maternal milk and supplementary blood)

2.3 Strategy for using information from existing programmes: Summary information on linkages and arrangements to other programmes utilized as data and/or information sources.

3. ANALYTICAL STRATEGY

Description of decision taken on the components of the annex substances that will be measured (analytes), description of decisions taken regarding analytical techniques and comparability (including inter-laboratory exchanges).

3.1 Strategy concerning analytical procedures

- Decisions taken regarding analytical techniques and comparability (including inter-laboratory exchanges)
- Protocols concerning extraction, clean-up, analysis, detection limits, and quality control.

3.2 Strategy concerning participating laboratories

- General description of the “tiered laboratory approach”
- Description of the “tiered laboratory approach” approach if used in the region and

identification of the laboratories involved.

4 ASSESSMENT STRATEGY

4.1 Data handling and preparation for the assessment

- Agreed protocols for data acquisition, storage, evaluation and access;
- The information warehouse;
- Data from existing programmes.

4.2 Preparation of the assessment reports.

- The final product of the GMP would be a compendium of regional assessment reports, one for each region, together with a global overview report.
- Regional assessments: Description of the arrangements put in place by the RIG to oversee the production of the substantive regional assessment for that region
- Identification of the roles and responsibilities of the drafting team of experts selected by the RIG to prepare the report for that particular region.
- Global assessments: Brief general description of the types of arrangements put in place by the GCG to oversee the production of the global report, which will be a synthesis overview of all of the regional reports.

5. RESULTS

5.1 The substances in context: Brief profiles of the chief characteristics of the annex substances including:

- Chemical identity;
- Persistence;
- Bio-accumulation/Bio-magnification;
- Properties related to long-range environmental transport;
- Status under the Convention;
- Historical and current sources;
- Regional considerations; and,
- Other information (e.g., trends in environmental levels reported elsewhere).

The above would be useful in both text and table format. The text should be organised in a common sequence (e.g., cyclodiene insecticides; DDT; toxaphene; hexachlorobenzene; PCB; PCDD and PCDF).

5.2 The results in context: A brief description of the nature of the first assessment. For many regions, the POPs GMP will be providing the first sets of available information. Therefore the detection of trends will not be possible. For those regions where trends are reported, a brief description of the statistical basis for the trend detection should be given.

5.3 Review of levels and trends in the region. A presentation of the results according to the levels (and when possible the detection of temporal trends) of the annex substances in each of the environmental media (compartments) included in the sample matrix. This approach for presentation is recommended because the interest of the COP is to be informed of the levels and trends of the annex substances rather than to be informed about what is happening with respect to individual media. Therefore the results would be provided in the following common sequence (cyclodiene insecticides); DDT; toxaphene; hexachlorobenzene; PCB; PCDD and PCDF). For example, the category of cyclodiene insecticides will be presented as levels and when possible as temporal trends in:

- Air
- Biota
    - Bivalves
    - Bird eggs
- Supplementary biota (fish and marine mammals)
- Human tissue (maternal milk and supplementary blood)

5.4 Brief overview of the relationship between the results and various indicators of significance relating to the environment and to human health. Article 16 does not request to be informed on the effects of the substances listed in the annexes. However, it is concerned with evaluating the effectiveness of the Convention in the context of which a simple comparison of the results on levels to various available and relevant indicators of significance would be useful (eg LOELs for similar species, and for humans, Tolerable Daily Intake Levels).

6. SUMMARY OF FINDINGS.
Under the proposed scheme, the GCG and the RIGs would consult to determine the nature of this section and would subsequently provide further guidance. The aim will be to provide a clear and concise synopsis of the results of the Global POPs Monitoring Programme for the use of the COP when it undertakes the Article 16 Effectiveness Review. It is suggested that it would be optimal for each regional summary to:

- Be restricted to three or four pages in length;
- Confined to reporting on the scientific observations: and,
- Avoid any hint of policy recommendations. It is for the latter reason that the word "summary" is used above rather than the word "conclusions".

It is recommended that the following approach be used. This is modelled upon assessments undertaken by the Intergovernmental Panel on Climate Change and by AMAP, which graduates the findings according to different levels of confidence. In the context of POPs, such a procedure could resemble the following:

- ***It has clearly been shown that***: Here you may expect to find information on levels and in some cases of temporal trends;

- ***There is convincing evidence that***: Here you may expect to find for example information on trends, and possibly on intra- regional and inter-regional transport.

- ***There are indications that***: Here you may expect to find for example information from modelling studies on intra- regional and inter-regional transport and on adverse effects comparisons (e.g. when the levels of POPs found in monitored species exceed levels where reports from the literature have indicated adverse effects in similar species).

DRAFT STRUCTURE OF THE GLOBAL REPORT

In order to assist both the global assessment process, and the critical review of the assessment by the Conference of the Parties, it is proposed that the global assessment would as far as is practical utilize the same internal structure as that found in the regional assessments.

1. INTRODUCTION
As in the draft structure of regional reports.

2. ORGANISATION
As in the draft structure of regional reports.

3. INFORMATION GATHERING STRATEGY.
As in the draft structure of regional reports.

3.2 Strategy for gathering new information:
As in the draft structure of regional reports.

3.3 Strategy for using existing information:
As in the draft structure of regional reports.

4. ANALYTICAL STRATEGY
As in the draft structure of regional reports.

4.1 Strategy concerning analytical procedures
As in the draft structure of regional reports.

4.2 Strategy concerning participating laboratories
As in the draft structure of regional reports.

5. ASSESSMENT STRATEGY
As in the draft structure of regional reports.

5.1 Data handling and preparation for the assessment
As in the draft structure of regional reports.

5.2 Preparation of the assessment reports. It has been suggested that the final product of the GMP would be a compendium of regional assessment reports, one for each region, together with a global overview report.

- **Regional assessments:** Brief general description of the types of arrangements put in place by the RIG to oversee the production of the substantive regional assessments;
- **Global assessments:** Description of the arrangements put in place by the GCG to oversee the production of the global report, which will be a synthesis overview of all of the regional reports;
- Identification of the roles and responsibilities of the drafting team of experts under the purview of the GCG that will prepare the global report. It would include identification of the individuals drawn from the writing teams of the regional assessments.

6. RESULTS

6.1 The substances in context: Brief profiles of the chief characteristics of the annex substances including:

As in the draft structure of regional reports, but the category of "regional considerations" would be replaced by one titled "global considerations".

6.2 The results in context:

As in the draft structure of regional reports.

6.3 Review of levels and trends in the global context. A brief synopsis presentation of the results reported in the Regional Assessment Reports according to the levels (and when possible the detection of temporal trends) of the annex substances in each of the environmental media (compartments) included in the sample matrix. This approach for presentation is recommended because the interest of the COP is to be informed of the levels and trends of the annex substances rather than to be informed about what is happening with respect to individual media. Therefore the results would be provided in the following common sequence (cyclodiene insecticides); DDT; toxaphene; hexachlorobenzene; PCB; PCDD and PCDF). For example, the category of cyclodiene insecticides will be presented as levels and when possible as temporal trends in:

- Air
- Biota
    - Bivalves
    - Bird eggs
- Supplementary biota (fish and marine mammals)
- Human tissue (maternal milk and supplementary blood)

6.4 Brief overview of the relationship between the results and various indicators of significance relating to the environment and to human health.

As in the draft structure of regional reports.

7. SUMMARY OF FINDINGS.

As in the draft structure of regional reports
but in a global context.

DRAFT STRUCTURE OF ENVIRONMENTAL LONG-RANGE TRANSPORT REPORTS

It is proposed that as soon as the Conference of the Parties has adopted the Global Monitoring Program, the GCG and the RIGs would develop a supplement to the Guidelines Document which would describe a guidance framework for the transport elements of the assessment.

It has been noted that the Global Report of the Regionally Based Assessment of Persistent Toxic Substances (GEF/UNEP 2000/3) included an assessment of knowledge on the long-range transport of these substances. The structure used in that study is considered to have functioned well and it is suggested that it could provide a first draft structure for a single transport report to serve both regional and global transportation elements as required under Article 16. This structure is provided here without modification to assist in planning and in the preparation of a report structure.

1. THE REASON FOR INTEREST IN ENVIRONMENTAL TRANSPORTATION PATHWAYS

2. COMPARISON OF THE ANNEX POPS FOR ENVIRONMENTAL TRANSPORTATION PATHWAYS

3. COMPARISON OF POPS ENVIRONMENTAL TRANSPORT BEHAVIOUR IN THE REGIONS

3.1 Region specific influences on atmospheric transport of POPs

3.1.1 Influence of airflow patterns on atmospheric transport of POPs

3.1.2 Influence of air-surface exchange and degradation on atmospheric transport of POPs

- Atmospheric degradation
- Atmospheric deposition
- Low latitudes
- Mid-latitudes
- High-latitudes

3.2 Region-specific environmental transport

- Influence of currents on oceanic transport
- Influence of particle settling and degradation on oceanic transport

3.3 Region-specific influences on riverine transport

3.4 Region-specific influences on transport by migratory animals

4 POPS ENVIRONMENTAL FATE AND TRANSPORT

4.1 Generic approaches to long-range environmental transport potential assessment

4.2 Regional approaches to long-range environmental transport potential assessment

- Spatially unresolved regional box models
- Spatially resolved regional box models
- Highly resolved meteorology-based regional transport models

4.3 Global approaches to long-range environmental transport potential assessment

- Spatially resolved global box models
- Highly resolved meteorology-based global environmental transport models

5 UNCERTAINTIES

6 SUMMARY

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GEF/UNEP, 2000/3 http://irptc.unep.ch/pts/

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